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A cellular automaton for the modeling of oscillations in a surface reaction

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The reaction of CO and O over a catalytic surface is studied with a cellular automata (CA) model. We extend the CA model proposed by Mai and von Niessen [Phys. Rev. A **44** R6165 (1991)] taking into account the variation of the temperature of the catalyst with the aim of analyzing the existence of oscillations in this reaction. The rate constants for different processes which govern the reaction are chosen in the Arrhenius form. Quasiperiodic, aperiodic, O-poisoned, and CO-poisoned regimes are observed depending on the temperature relaxation parameter. The results from the CA model presented are in agreement with several oscillatory behaviors which the catalyzed oxidation of CO exhibits. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1770455]

I. INTRODUCTION

The oxidation of CO by O_2 over group VIII metal catalysts (Pt, Pd, or Ir) is one of the most intensely studied heterogeneous catalytic reactions.[2–4] This reaction, as a good example of nonequilibrium systems, exhibits kinetic phase transitions, bistability, and associated hysteresis, and a rich variety of oscillatory behaviors, which vary from periodic to quasiperiodic and to aperiodic.

Most models proposed to describe an oscillatory behavior in the catalyzed oxidation of CO involve nonlinearities of different natures. For example, models, where the reaction heats generated on the catalyst may be distributed over the surface much faster than they are dissipated in the ambient and, therefore, the temperature of the catalyst can be maintained different from its surroundings, have been considered. In these models, temperature oscillations are jointly originated with concentration oscillations. Thermokinetic oscillations arise due to the highly nonlinear dependence of the reaction rate upon the temperature.

One of the first models to describe the appearance of temperature oscillations was proposed by Lagos, Sales, and Suhl.[5] On the basis of mean-field theory, they obtained the kinetic equations by using the singlet closure approximation and assuming that the surface is a square lattice. They formulated the kinetics of the reaction by an autonomous system of three nonlinear differential equations in terms of the CO and O coverages, and the surface temperature. Their numerical solutions are in qualitative agreement with experiments carried out by Dauchot and Van Cakenberghe.[6] The mechanism proposed by these experimenters to explain the appearance of thermokinetic oscillations is the following: (a) Adsorption of O_2 is favored over that of CO by an increase in temperature of the catalyst. Thus, starting from the hot surface, O_2 has been mostly adsorbed. (b) As the surface cools down (its surroundings are at a constant and different temperature), CO is progressively adsorbed and the reaction proceeds rapidly. (c) The CO is eliminated by the Langmuir-Hinshelwood (LH) mechanism and the hot surface resulting

from that exothermic reaction is again covered primarily and rapidly with O_2.

Lagos *et al.* did not consider the role played by desorption of reactives and they neglected the temperature dependence of the LH mechanism. Only the adsorption of O_2 was assumed to be temperature dependent. It seems that the conditions for the occurrence of oscillations in this model[5] are far from the experimental conditions, because those assumptions made such model less realistic.[7,8] However, the simple structure of the model of Lagos *et al.* is amenable to a simple bifurcation analysis. Stability analysis of the model has also revealed that oscillatory behavior is obtained only for certain values of the parameter that controls the decay of temperature fluctuations of the surface. An interesting result obtained from their[5] mathematical analysis is that, in the oscillatory state, the average yield of the reaction product may be greater than the yield in the corresponding steady state; in this way, efficiency of catalyst is improved.

In another paper, Lagos, Simoes, and Godoy[9] generalize the kinetic model previously developed by them,[5] incorporating an experimentally observed ''slow'' suboxide kinetic step. Their results are in agreement with experimental data: stable, oscillatory, and quasiperiodic regimes are obtained.

The catalyzed oxidation reaction of CO was also studied by Ziff, Gulari, and Barshad[10] (ZGB model). These authors studied the reaction via Monte Carlo simulations on a square lattice and found three zones with regard to the fraction of CO molecules in the gas phase, y_{CO}. For low values of y_{CO}, $y_{CO} < y_1 = 0.389$, the CO pressure is low compared to the O_2 pressure and, as a consequence, the catalyst is poisoned by O_2. For $y_1 < y_{CO} < y_2 = 0.525$, the CO adsorption competes with oxygen adsorption, and the CO_2 production increases with CO pressure. Therefore, there is a reactive steady state where CO_2 molecules are continuously produced. The transition at y_1 is a second-order (continuous) kinetic phase transition. For $y_{CO} > y_2$ the O_2 pressure is low compared to the CO pressure, and the catalyst is poisoned by CO. The kinetic phase transition at y_2 is of first order, because the CO_2 production rate changes discontinuously.

Luque[11] studied the CO oxidation reaction on the basis

of ZGB model. He derived the kinetic equations by starting from a master equation, following the generalized Glauber-Ising model. Since the distribution of adsorbed particles on the surface can affect the transition probabilities in the adsorption and desorption processes, the spatial correlations were considered, and larger clusters that involved up to eight sites were introduced. A set of five nonlinear kinetic equations was obtained for the densities of $CO (n_{CO})$ and atoms $O (n_O)$, and pairs CO-$CO (n_{CO\text{-}CO})$, CO-$O (n_{CO\text{-}O})$, and O-$O (n_{O\text{-}O})$ considering a doublet closure approximation. In addition to the three zones obtained by Ziff, Gulari, and Barshad, a bistability zone was found: one reactive stable state producing CO_2 and another in which the catalyst is poisoned by CO; depending on initial conditions, the reaction will evolve towards one of the stable stationary states.

On the basis of the results obtained by Lagos, Sales, and Suhl[5] and in order to study the oscillatory behavior of the reaction, Luque's model[11] was extended by us by adding an equation for the rate of change of the surface temperature.[12] The results demonstrate that the nonlinearity introduced in the model gives rise to multiple stable stationary states and oscillations for certain values of the temperature relaxation parameter and other operating condition parameter. In the bistability zone, one reactive state producing CO_2 and another in which the catalyst is poisoned by CO are found. The new reactive state can be either a stable node or an oscillatory state, and appears only for certain values of the temperature relaxation parameter. Thus, as in other models, this parameter plays an important role in the onset of oscillations.

In addition to the use of mean-field theory and Monte Carlo (MC) simulation for the study and modeling of heterogeneous catalytic systems, recently the technique of cellular automata[13] (CA) is another possibility to simulate the oscillatory behavior of the oxidation of CO on metallic surfaces with the advantage that the CA approach, faster than MC simulations, may become equivalent to the latter. A cellular automaton consists of a discrete number of cells or sites which evolve in discrete time steps following the same deterministic (or probabilistic) rules. These simple transition rules can be easily programmed. In the course of the temporary evolution each cell can only adapt values from a finite set. The rules for the evolution of a cell only depend on the state of the cells in the local neighborhood. At each time step the value of each site is updated. This feature allows parallel processing and results a substantial reduction in the computational time. Physical, chemical, and biological systems with many discrete elements and with local interactions can be modeled using CA. A survey of recent literature indicates that the study of surface chemical reactions with CA is possible. So, there is a study of the ZGB model by Mai and von Niessen.[1] They introduce a CA approach which describes the steps of adsorption and reaction correctly and obtain a good quantitative agreement with the ZGB model. Later, Tambe, Jayaraman, and Kulkarni,[14] following Mai–von Niessen CA model, formulate CA transition rules for the catalytic oxidation of CO incorporating the Eley-Rideal (ER) step, that is, the reaction between CO in the gas phase with the atomic adsorbed oxygen. In this paper, we extend the CA proposed by Mai and von Niessen[1] in order to analyze the existence of thermochemical oscillations in the case of CO oxidation. In this way, we can compare the results obtained by us in a previous article[12] with the ones computed here via CA simulations.

In the following section, the cellular automaton model of Mai and von Niessen is extended by adding an equation for the rate of change of the surface temperature. The results of our simulations are described in Sec. III and discussed in the light of mean-field solutions obtained in a previous paper. The conclusions and future developments of CA model presented here are summarized in the last section.

II. THE MODEL

The surface of the catalyst is represented as a two-dimensional square lattice with periodic boundary conditions. The assumption is that the molecules of carbon monoxide CO(ads) and the oxygen atoms O(ads) both occupy single active sites on the lattice, where ''ads'' indicates that the species is adsorbed on the surface. The carbon monoxide and oxygen molecules, CO(gas) and O_2(gas), collide randomly on the surface and when there is an available site they are adsorbed. Thus, gaseous CO(gas) and O_2(gas) can competitively be adsorbed on the same active sites. Two adjacent sites are needed for the oxygen molecule O_2(gas) to be adsorbed. Upon adsorption, the O_2(gas) dissociates into two O atoms, each one residing on a separate surface site. When a molecule is adsorbed on the surface, it becomes fixed, so that superficial diffusion is ignored in this model. If a CO(ads) molecule is a neighbor of an O(ads) atom, the reaction occurs and the product molecule CO_2 is desorbed as soon as it is formed. The model assumes that the reaction takes place according to three basic steps:

$$CO(gas) \rightarrow CO(ads), \tag{1}$$

$$O_2(gas) \rightarrow 2O(ads), \tag{2}$$

$$CO(ads) + O(ads) \rightarrow CO_2(gas). \tag{3}$$

The reaction between dissociatively adsorbed oxygen and adsorbed CO, process (3), is known as the LH mechanism. The rate constants k_i, for each one of three kinetic mechanisms named above ($i=1$, adsorption of CO; $i=2$, adsorption of O_2; $i=3$, desorption of CO_2), are chosen in the Arrhenius form:

$$k_i = A_i \exp\left(-\frac{E_i}{k_B T}\right),$$

where A_i are frequency factors, k_B is the Boltzmann constant, T denotes the temperature of the surface, and E_i are activation energies of each one of the three elemental processes. These energies correspond to the action of the substrate and are assumed to be coverage independent. With the aim of studying the oscillatory behavior of the reaction, the model must be supplemented by the addition of an equation describing the variation of the surface temperature due to the adsorption and reaction processes:

$$C\frac{dT}{dt} = -L(T-T_B) + \sum_{i=1}^{3} \Delta H_i p_i,$$

where C is the heat capacity of the catalyst, L is the heat transfer coefficient (L is approximately equal to thermal conductivity multiplied by a geometric factor), T_B is the room temperature, ΔH_i are the reaction heats of the processes (1)–(3), including also a suitable geometric factor, and p_i are the number of processes of type i which take place per unit area. The previous equation can be written as

$$\frac{dT}{dt} = -\gamma(T-T_B) + \sum_{i=1}^{3} h_i p_i, \qquad (4)$$

where $\gamma = L/C$ is the dissipative factor or the relaxation rate of T to T_B and $h_i = \Delta H_i/C$. Thus, the linear term $-\gamma(T-T_B)$ describes the dissipation heat from the catalyst surface towards its surroundings, while $\sum_{i=1}^{3} h_i p_i$ is the net heat generated on the catalyst surface in the reaction steps. The model can give rise to oscillatory behavior for certain values of the set of parameters $\{A_i, E_i, h_i, \gamma\}$, room temperature being at $T_B = 300$ K. The kinetics of the reaction is described in terms of the density of adsorbed particles of CO and O, n_{CO} and n_O, the production of CO_2, R, that is, the density of pairs CO-O which are formed and leave the surface immediately after its formation, and, finally, the surface temperature T, which differs from the temperature of the gas. Let us emphasize the difference between the ambient temperature T_B, which is essentially constant in time, and the surface temperature T of the catalyst. The model involves the surface temperature as a dynamical variable. The variation of this surface temperature, being subject to Eq. (4), can lead to thermal instabilities because the dependence of the different reaction steps (1)–(3) upon the temperature at Arrhenius law is the main feedback mechanism generating oscillations. We follow Mai and von Niessen in the cellular automaton procedure. The CA uses a square lattice with $N = L \times L$ cells. To overcome problems with the stoichiometry of the chemical reaction, the lattice is divided into Margolus blocks containing 2×2 cells as elementary cells. All the cells in the Margolus block are simultaneously updated following a probabilistic rule. After one sweep through the lattice, the Margolus block is shifted by one cell to the right, then down, then left, and then up to get all the different configurations. In the Mai–von Niessen model the transition probabilities of the CA depend on the initial state of the cells, on the statistical weights of the individual configurations, which are taken as classical, and on the mole fractions of the gaseous reactants, y_{CO} and y_O, where $y_O = 1 - y_{CO}$. CA transition rules are shown in Fig. 1. For each initial state, the sum of all transition probabilities is normalized to 1. In our model, y_{CO} is defined as the relative rate of potentially efficacious collisions of CO molecules on the surface; that is, $y_{CO} = k_1/(k_1 + k_2)$, meanwhile $y_O = k_2/(k_1 + k_2)$. According to the ZGB model, the probability of reaction between pairs CO-O, process (3), is assumed to be unity.

III. RESULTS

Initially the problem was complicated, since describing the reaction requires many parameters. In this paper, we want to compare the cellular automata simulations with the results
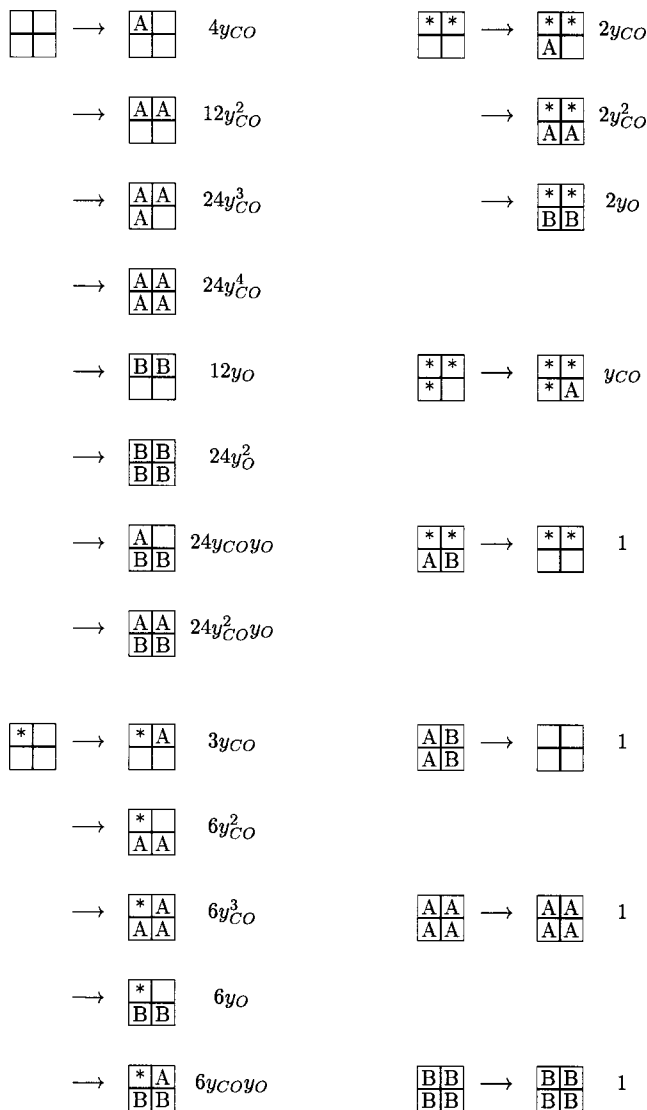

FIG. 1. Cellular automata transition rules for the CO+O_2 reaction. A denotes a CO molecule, B an oxygen atom, and $\star$ any occupied site. The transition probabilities of CA depend on the initial state of the cells, on the statistical weights of the individual configurations, which are taken as classical, and on the mole fractions of the gaseous reactants, y_{CO} and y_O, where $y_O = 1 - y_{CO}$. In the model, y_{CO} is defined as $y_{CO} = k_1/(k_1 + k_2)$, where $k_i = A_i \exp(-E_i/k_B T)$. For each initial state, the sum of all transition probabilities is normalized to 1.

previously analyzed by us, starting from the kinetic equations obtained by using a mean-field approximation type.

According to experimental data, it seems that oscillations occur under the conditions where oxygen adsorption is the main mechanism. Therefore, we assume that the adsorption of CO and the reaction between O and CO on the surface are unactivated processes, $E_1 = 0$, $E_3 = 0$; the adsorption of O_2 is the only activated process. We make a minor simplification considering that the reaction heat for the adsorption of O is twice the value of that of the CO and the reaction heat for CO_2 is negligible, and so $h_2 = 2h_1$ and $h_3 = 0$. We have fixed the values $A_1 = 0.05$, $A_2 = 4 \times 10^5$, $A_3 = 1$, $E_1 = 0$, $E_2/k_B = 6000$, $E_3 = 0$, $h_1 = 150$, $h_2 = 300$, and $h_3 = 0$ (in arbitrary units), which have been used in Ref. 12, where the temperature relaxation parameter γ is the control parameter.

The simulation was started with an empty lattice of 256 $\times$256 sites with periodic boundary conditions. In most cases the regimes have been reached after 2000 time steps. However, for the transitions from aperiodic regime to quasiperiodic behavior and from this to poisoning of the surface by CO, 12 000 and 6000 time steps were necessary, respectively. To assure the validity of our simulations we have used four different series of random numbers in each simulation, yielding essentially the same results.

For each value of γ, the simulation consisted of 2000 iterations over the entire lattice. After one sweep through the lattice, the Margolus block is shifted by one cell to the right, then down, then left, and finally up. Therefore, an iteration (time step) consists of four sweeps over the complete lattice. After each iteration, the number of adsorption processes of CO and O, and the number of Langmuir-Hinshelwood events were counted and the surface temperature was modified according to Eq. (4). The data output show the temperature of the catalyst surface, T, the coverages fractions of CO and O, n_{CO} and n_O, and the number of pairs CO-O which are formed per unit area, R, in each iteration over the entire lattice.

Oscillating regimes are obtained in the transition region where the surface changes from a complete coverage by oxygen to a complete coverage by CO molecules. The poisoning of the surface of the catalyst by CO or O occurs at room temperature, $T_B = 300$ K. Depending on the temperature relaxation parameter γ, we obtain a region where the catalyst is not poisoned: $0.005 \leq \gamma \leq 0.27$. In this range there is either an aperiodic regime between the limits $0.005 \leq \gamma \leq 0.09$ or a quasiperiodic behavior for $0.10 \leq \gamma \leq 0.27$. In both cases, the surface temperature fluctuates around a value greater than ambient temperature, favoring in this way the adsorption of O_2 and decreasing the adsorption of CO. This fact shows that the CO_2 production is favored. On the other hand, for $0 < \gamma \leq 0.004$, the surface is quickly poisoned by atoms of O at room temperature and, therefore, the reaction between CO molecules and O atoms is not possible. The same situation happens for $\gamma \geq 0.28$, where the surface is covered slowly with CO, thus producing poisoning of the catalyst by this reactant.

Our CA model is able to describe a richer variety of behaviors (quasiperiodic, aperiodic, and two poisoned states) than within the mean-field approximation. There, and for all values of γ, there was a state corresponding to complete coverage with CO at room temperature, which is a stable node. Besides this state, a new solution was obtained via mean-field approximation when the values of γ varied. This new state can be either a periodic oscillatory state in the range $0.10 \leq \gamma \leq 0.15$ (the temperature fluctuates around a greater value than ambient) or a stable node for $0.03 \leq \gamma \leq 0.09$, corresponding to a reactive steady state producing CO_2 at a greater temperature than room temperature. Quasiperiodic, aperiodic, and O-poisoned states were never obtained by mean-field approximation.

To study qualitatively the system behavior, we use the Poincaré's map, also known as the iterative map. If the behavior is periodic with a single frequency, the Poincaré's map will show a single point. On the other hand, if the be-

havior is aperiodic, the points will appear on the map in a scattered way, not following any recognized line and filling up the iterative map. Finally, if the behavior is quasiperiodic, the points densely populate an invariant closed curve.

Figure 2 shows the time series of T, n_{CO}, n_O, and R for two values of γ. It is also shown the corresponding iterative map for each variable. For $\gamma = 0.20$, the Poincaré's map shows a quasiperiodic behavior: the points are put on a same closed curve perfectly defined. However, for $\gamma = 0.01$, the aperiodic behavior can be observed.

Quasiperiodic behavior of the oscillations of the catalyst temperature, coverage fractions of CO and O, and CO_2 production for $\gamma = 0.20$ are shown in Fig. 3. Different frequencies of the quasiperiodic regime can be observed.

Between $0.10 \leq \gamma \leq 0.27$, corresponding to quasiperiodicity, the oscillation amplitude and the size of the iterative map increase as γ increases. This is shown in Fig. 4, where it can be seen that the average production of CO_2 is favored as γ increases. At $\gamma = 0.28$, the quasiperiodic regime disappears and the surface remains poisoned by CO at $T_B = 300$ K.

Finally, Fig. 5 shows the four regimes which are found in the CA model. For $\gamma = 0.004$, the catalyst is saturated by adsorbed oxygen after a transient time. The state obtained for $\gamma = 0.07$ is an aperiodic state where the temperature of the surface fluctuates around a greater value than room temperature and a small production of CO_2 is obtained due to that the surface is not saturated by any of the reactive species. For $\gamma = 0.15$, the oscillatory behavior is quasiperiodic and the amplitude of the oscillations is greater than the previous state ($\gamma = 0.07$), thus increasing the averages of the densities of CO and O, the yield of CO_2, and the surface temperature. For $\gamma = 0.28$, the surface is covered slowly with CO, thus producing poisoning of the catalyst by this reactant. It can be also observed that the amplitude of the oscillations starts to decrease slowly until the catalyst surface is poisoned suddenly by CO molecules at ambient temperature.

IV. CONCLUSIONS

In short, we have presented a CA model, extension from the Mai–von Niessen model,[1] that includes the temperature as a dynamic variable with the purpose to model the oscillatory behavior of reaction of CO. The nonlinear dependence of the rate constants on the temperature given by the Arrhenius law introduced in the CA model gives rise to quasiperiodic and aperiodic behaviors for certain values of the temperature relaxation parameter. As in others models, this parameter plays an important role in the onset of oscillatory regimes.

We think that the flexibility of the CA model presented here allows us to continue studying this surface's chemical reaction. Future works will analyze the effects of the addition of the Eley-Rider step, the inclusion of defects on the surface, and the Langmuir-Hinshelwood as an activated process, among others topics.
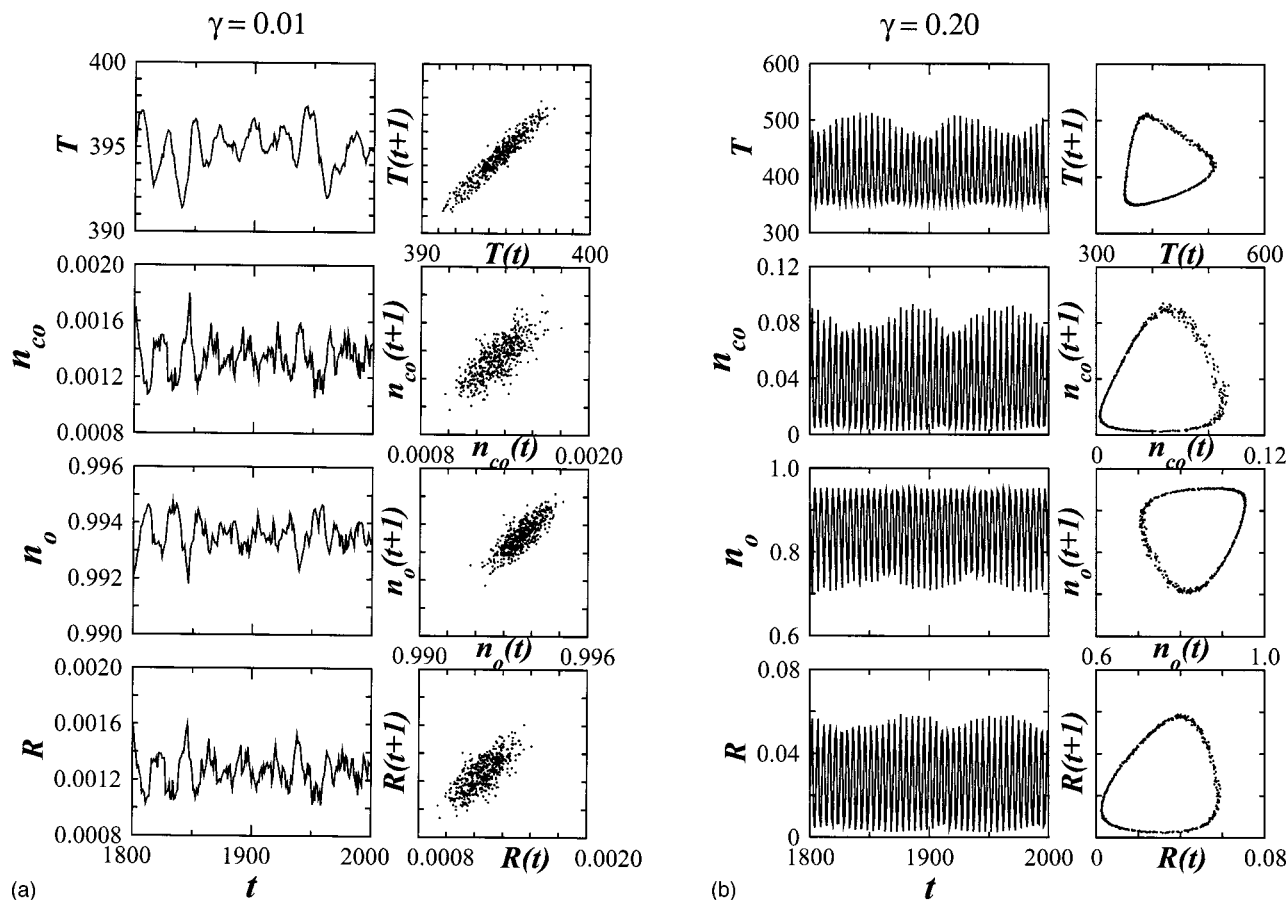
FIG. 2. Time series of the surface temperature, T (in Kelvin), dimensionless coverage fractions of CO and O, n_{CO} and n_O, and the production of CO_2, R [defined as the number of process of type (3) which take place per unit area], for two values of the control parameter γ. The time series of the CA simulations show aperiodic and quasiperiodic regimes. (a) For $\gamma=0.01$, the regime is aperiodic as can be observed in "filled space" from the Poincaré's maps. (b) For $\gamma=0.20$, the Poincaré's maps show a quasiperiodic behavior.
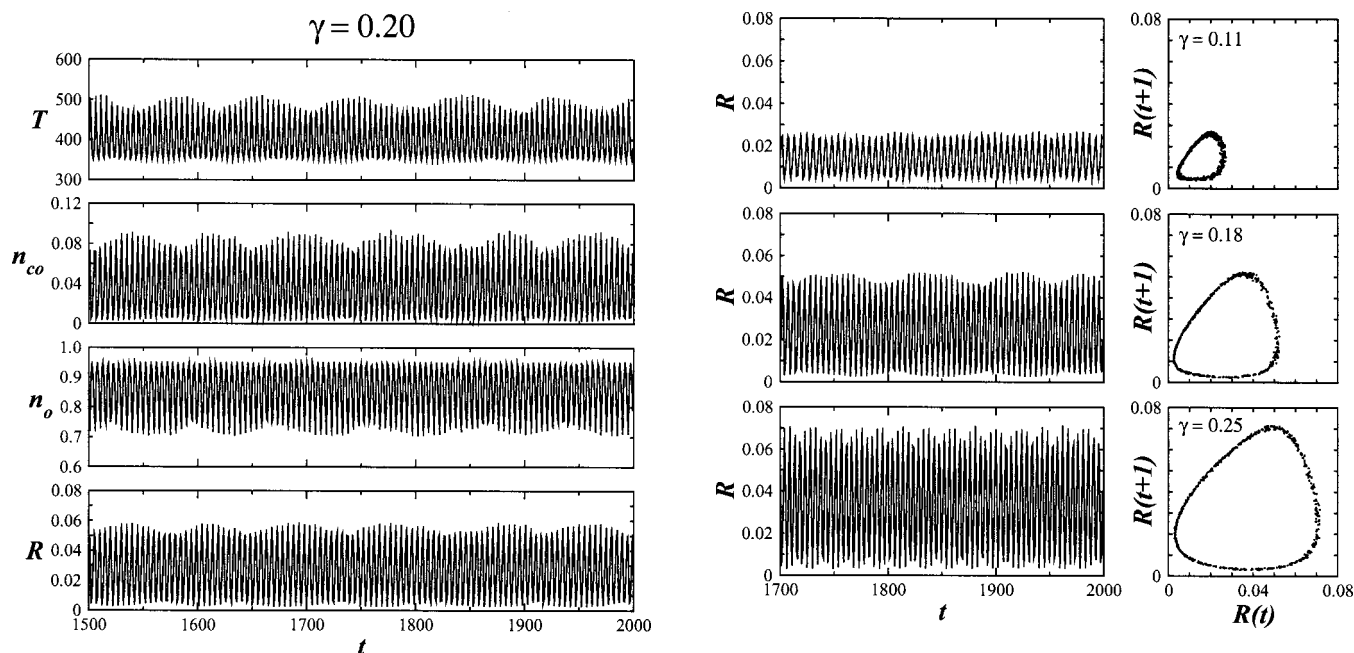

FIG. 3. Temporal behavior of the surface temperature (in kelvins), densities of CO and O, and production of CO_2 for $\gamma=0.20$. This state corresponds to the region where the system behavior is quasiperiodic.

FIG. 4. Development of the oscillations of the reaction product CO_2 and the associated Poincaré's maps for different values of γ. As can be seen, the oscillation amplitude and the size of the Poincaré's map increase as γ increases, thus favoring the average yield of CO_2.

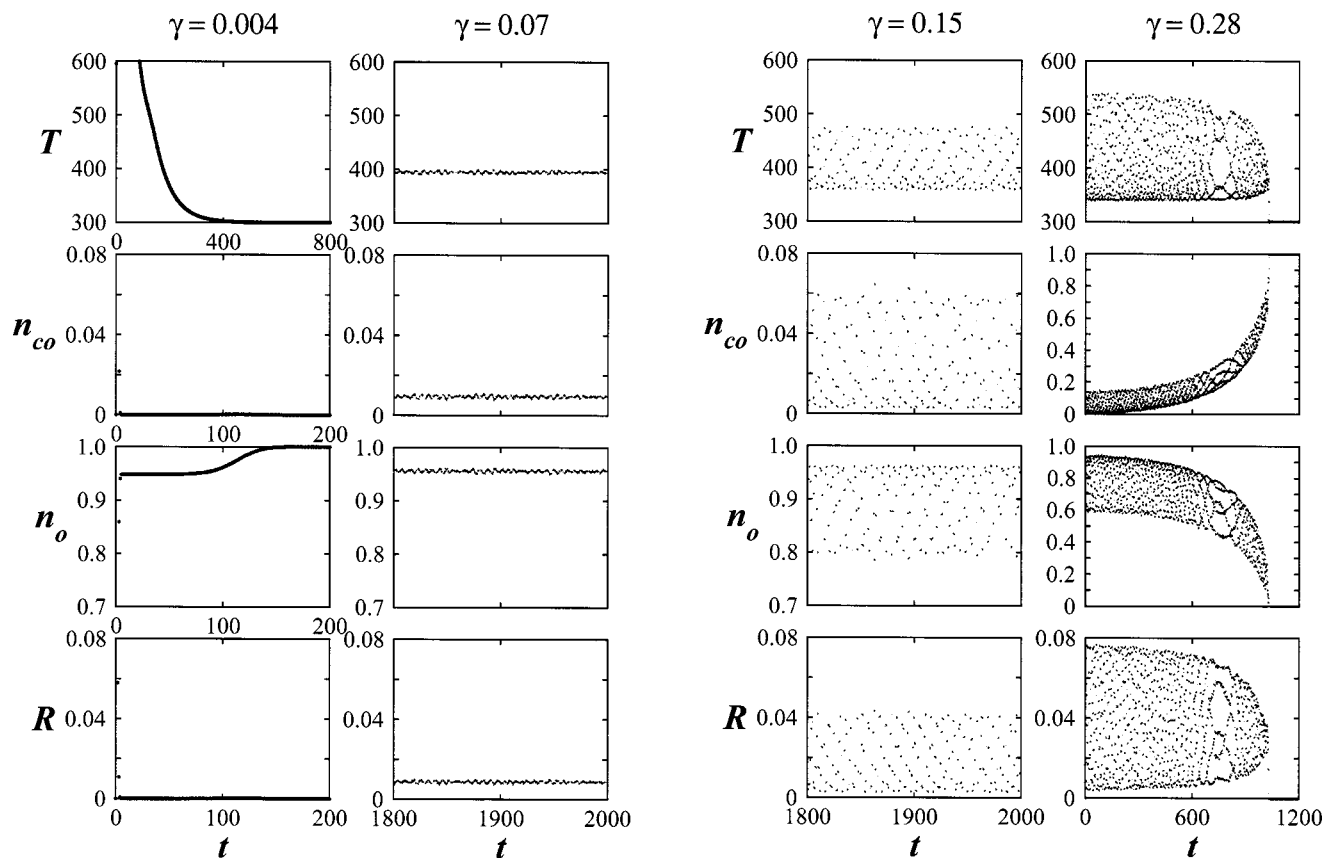FIG. 5. Results obtained from cellular automaton simulations as a function of the control parameter γ. The graphs show the temporal behavior of the system. (a) For $\gamma=0.004$, the surface is poisoned quickly by atoms of O. For $\gamma=0.07$, there is an aperiodic state. (b) For $\gamma=0.15$, the behavior of the system is quasiperiodic and, finally, for $\gamma=0.28$, the surface is poisoned by CO. In the poisoned states, the catalyst surface remains at room temperature, $T_B = 300$ K, while in the oscillatory regimes the surface temperature fluctuates around a temperature greater than T_B.

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