PHYSICAL REVIEW E **74**, 016208 (2006)

Stabilization from chaotic to periodical states in a model of cellular automaton for oxidation of CO

A. Córdoba, M. C. Lemos, and F. Jiménez-Morales
Departamento de Física de la Materia Condensada, Universidad de Sevilla, P. O. Box 1065, 41080 Sevilla, Spain

(Received 4 April 2006; published 18 July 2006)

The chaotic behavior of a chemical reaction can be controlled perturbing periodically some of the parameters externally governing the reaction. Based on the resonance phenomenon, the method of external forcing can convert chaotic behavior into a periodical one through the application of a sinusoidal modulation. In this paper we analyze the effect of a periodical perturbation on room temperature in a model of cellular automaton that studies catalytic oxidation of CO. This model considers the reaction of carbon monoxide and oxygen adsorbed on a surface allowing the variation of the surface temperature and analyzing the time oscillations in the reaction. The results of simulations of this model show quasiperiodical and chaotic behaviors. Then the strategy of control through periodical forcing is able to remove the chaotic dynamics by means of the stabilization of periodical solutions, there being enough of a perturbing harmonic function with only one frequency to transform a chaotic state of the system into a periodical state with periodicity 1.

DOI: 10.1103/PhysRevE.74.016208 PACS number(s): 05.45.Gg, 05.45.Tp, 82.20.Wt

I. INTRODUCTION

Oxidation of carbon monoxide by oxygen on catalytic metals, such as platinum, palladium, or rhodium, is one of the best studied heterogeneous catalytic reactions. [1,2] This reaction, as a good example of a system far from thermodynamic equilibrium, exhibits kinetic phase transitions, bistability and hysteresis, and a rich variety of oscillatory behaviors, ranging from periodical evolution to quasiperiodical and chaotic ones.

Most models proposed to describe oscillatory behavior in the oxidation of CO involve nonlinearity of different types. There are models in which the catalyst temperature has a different value than the environment temperature, because the reaction heat can spread on the surface more quickly than it transfers to the milieu, causing fluctuations in the surface temperature. These oscillations, called thermokinetic to distinguish it from isothermal ones, in which surface temperature remains constant, are due to a strong nonlinear dependence of the reaction rate on temperature. To carry out the study of these oscillations one must include in the model an equation describing the time change of the surface temperature.

The methods most frequently used to model kinetics of this kind of chemical reactions have been kinetic equations obtained through mean-field approximations and the Monte Carlo (MC) method. More recently, techniques of cellular automata [3] (CAs) have shown to be efficient tools for simulating the behavior of catalytic systems, being equivalent to the MC method and quicker. A CA consists of a lattice, in which sites can be in a finite number of states and which evolve into discrete time steps according to determinist or probabilistic rules. The transition rules for a cell depend on the states of the cell and its neighbors, are the same throughout the lattice and can be easily programmed. The value of the state of each site is updated for each time step. The CAs allow parallel processing without any difficulty, and this fact substantially reduces the computation time. Some surface chemical reactions have been modeled using CAs. [4–10] Recently Jiménez-Morales and Lemos have used a CA to study the oscillatory behavior in the oxidation reaction of CO, including the surface temperature as a variable, and the results showed different chaotic and quasiperiodical regimes. [11,12]

The attempts to control chaos are relatively recent, and there are a great number of publications about it. [13] The periodical forcing of the kinetics of a reaction through the variation of an external parameter, as, for example, the rate of some elementary process or the bath temperature, is one of the most used tools for controlling chaos in basic and applied studies of heterogeneous catalytic processes. [14] So, in experiments focused on the study of oscillatory catalytic reactions, periodical perturbations are applied to stabilize oscillations of period 1 (P1). This stabilization is easily reached if both external and internal frequencies coincide. Aperiodic or chaotic natural kinetic oscillations can also be stabilized to periodical ones by means of periodic perturbations. Through the application of the external forcing technique, one tries to stabilize unstable periodical orbits contained in chaotic attractors of the system.

In this paper we want to clarify the influence on the oscillatory behavior to be found in the oxidation of CO of forced periodical variations on environment temperature, analyzing the results obtained from a CA simulation. Thus, in Sec. II we describe the model of reaction and preliminary results obtained with the CA, and in Sec. III consider the periodical modulation imposed to the system. Finally, in Sec. IV some conclusions are summarized.

II. THE MODEL

The model assumes that the reaction proceeds according to three elementary mechanisms

$$\mathrm{CO(gas)} + V \rightarrow \mathrm{CO(ads)}, \qquad (1)$$

$$\mathrm{O_2(gas)} + 2V \rightarrow 2\mathrm{O(ads)}, \qquad (2)$$

$$\mathrm{CO(ads)} + \mathrm{O(ads)} \rightarrow \mathrm{CO_2(gas)} + 2V, \tag{3}$$

where (ads) indicates that the particle is adsorbed on the surface and V denotes a vacant site. Two adjacent vacant sites are necessary for an oxygen molecule to be adsorbed. When a molecule is adsorbed on the surface, it remains fixed on it, and therefore surface mobility is ignored in this model.

The rates, k_i, for each process mentioned above ($i=1,2,3$) are chosen in the Arrhenius form

$$k_i = A_i \exp\left(-\frac{E_i}{k_B T}\right), \tag{4}$$

where A_i are frequency factors, k_B is the Boltzmann constant, T denotes the surface temperature, and E_i are the activation energies associated to the elementary processes.

In order to study the oscillatory behavior of the reaction, an equation describing the variation of the surface temperature due to the adsorption and reaction processes must be considered

$$\frac{dT}{dt} = -\gamma(T - T_B) + \sum_{i=1}^{3} h_i p_i, \tag{5}$$

where γ is the relaxation coefficient of the surface temperature towards the environment temperature, T_B, and h_i and p_i are the reaction heats of the processes (1)–(3) and the number of processes of i kind taking place per unit area, respectively.

The model can give rise to oscillatory evolution for certain values of the parameter set $\{A_i, E_i, h_i, \gamma, T_B\}$. The reaction kinetics is described in terms of the densities of adsorbed molecules CO, n_{CO}, and atoms O, n_{O}, the production of $\mathrm{CO_2}$, R, that is, the density of pairs CO-O that are formed and leave the surface immediately after its formation, and, finally, the surface temperature T, which differs from that of the environment, T_B. The variation of the surface temperature, governed by Eq. (5), along with the coupling with the rates in Eq. (4), can lead to thermal instability, oscillations and chaos.

The model of CA uses a square lattice with $L \times L$ cells and follows the guidelines proposed by Mai and Niessen. [4] To avoid problems with the stoichiometry of the chemical reaction, the lattice is divided in Margolus blocks, which contain 2×2 cells each. Any cell in a Margolus block (MB) is the neighbor of three other cells. Using this definition, the CA transition rules for reaction steps (1)–(3) can be easily formulated. In the Mai-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 ones, and on the mole fractions of the gaseous reactants, y_{CO} and y_{O}, where the $y_{\mathrm{O}} = 1 - y_{\mathrm{CO}}$. CA transition rules are shown in Fig. 1. For each initial state, the sum of all the 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, $y_{\mathrm{CO}} = k_1/(k_1 + k_2)$, meanwhile $y_{\mathrm{O}} = k_2/(k_1 + k_2)$. Also, the probability of formation of $\mathrm{CO_2}$ from an adsorbed CO-O pair, given by Eq. (3), is assumed to be 1.

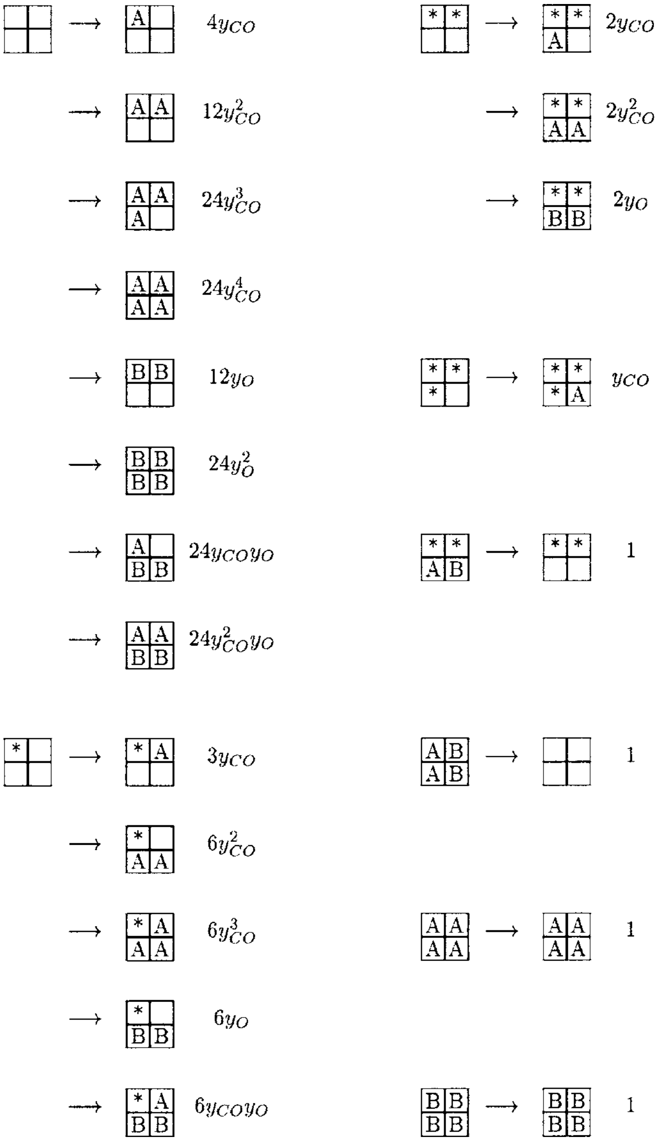

FIG. 1. Transition rules of the CA for the reaction of oxidation of CO. A denotes a CO molecule, B an oxygen atom, and * any occupied site. The transition probabilities of the CA depend on the initial state of the cells, on the statistical weights of the individual configurations, which are taken as classical, and on the mole fractions of the gaseous reactants, y_{CO} and y_{O}, where $y_{\mathrm{O}} = 1 - y_{\mathrm{CO}}$. In the model, y_{CO} is defined as $y_{\mathrm{CO}} = k_1/(k_1 + k_2)$, 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.

With the aim of understanding CA evolution rules, let us consider the possibilities of transition of a MB with two examples. First, the probability of the adsorption of one CO molecule into an empty MB depends on the probability of selecting a CO molecule from the gas phase (y_{CO}) and on the number of vacant cells in the MB that determines the number of different adsorption states. In an empty MB there are four different possibilities. Therefore the (unnormalized) probability for this event is 4 y_{CO}. Only one of the possible configurations is shown in Fig. 1. Second, let us consider a MB with two occupied cells. The possibilities for the evolution of this MB are: (1) one CO molecule can be adsorbed, (2) two

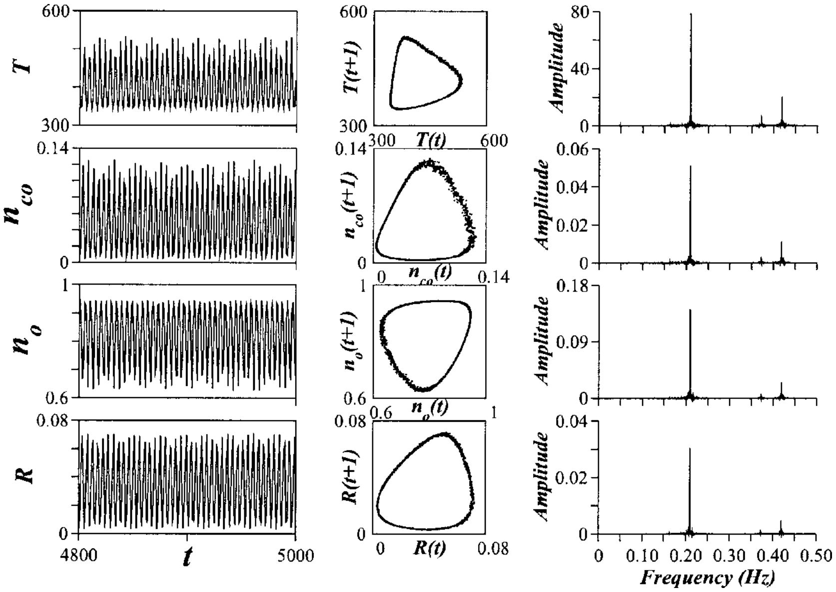

FIG. 2. Time series of the autonomous oscillations (without forcing) of the surface temperature, densities of CO and O, and production of CO_2, for $\gamma=0.25$. These series, obtained by simulations of the CA, show a quasiperiodical behavior, as it can be observed in the Poincaré maps and the Fourier spectra attached. The points are allocated on an iterative map on the same closed curve. The Fourier spectrum is discrete with two fundamental frequencies corresponding to the peaks 0.209 47 Hz and 0.371 34 Hz, because the third peak is a harmonic of the first fundamental frequency, $2f_0=0.418\ 95$ Hz.

CO molecules can be adsorbed, and (3) one oxygen molecule can be adsorbed dissociatively into the two empty cells. The corresponding transition probabilities are: 2 y_{CO}, 2 y_{CO}^2, and 2 y_O. The coefficients indicate the possible ways in which the particles can be placed in that particular MB. Each MB is changed during one sweep through the whole lattice and all MBs are updated simultaneously.

The simulation was started with an empty lattice (zero CO and O coverages, and $T=T_0$, near to T_B) of 256×256 sites with periodic boundary conditions. The first step in transforming the MBs is the examination of its present state. This decides the group of possible transitions that the MB can make. Next, a random number is generated, and thereby a specific transition for the current MB is selected. The state of each cell in a MB is modified accordingly and the procedure is repeated for all the MBs. Such a CA is called a probabilistic CA. Starting from here, the variation of the surface temperature is implemented in the CA model. In the Mai-Niessen model y_{CO} is independent of temperature, but in our model $y_{CO}=y_{CO}\ (T)$. After covering the entire lattice with the MBs, the number of processes of the i kind taking place per unit area p_i [processes (1) to (3)] is counted, and the surface temperature is modified according to equation $T=T_0-\gamma(T-T_B)+\Sigma_{i=1}^{3}h_ip_i$. After one sweep through the lattice, the MBs are shifted by one cell to the right and a new sweep is performed; next the MBs are shifted to a cell down, then left, and then up, to get all the possible configurations inside a MB. The surface temperature is changed in each sweep according to the equation mentioned above. Therefore, a time step consists of four sweeps over the complete lattice. After each time step, the surface temperature T, the coverage fractions of CO and O, n_{CO} and n_O, and the number of pairs CO-O which are formed per unit area, R, were obtained.

In our simulations, we have fixed the values $A_1=5\times10^{-2}$, $A_2=4\times10^5$, $A_3=1$, $E_1=0$, $E_2/k_B=6\times10^3$ K, $E_3=0$, $h_1=150$, $h_2=300$, $h_3=0$, and $T_B=300$ K as room temperature, γ being the control parameter. For each value of γ, the regimes have been reached after 2000 time steps in most

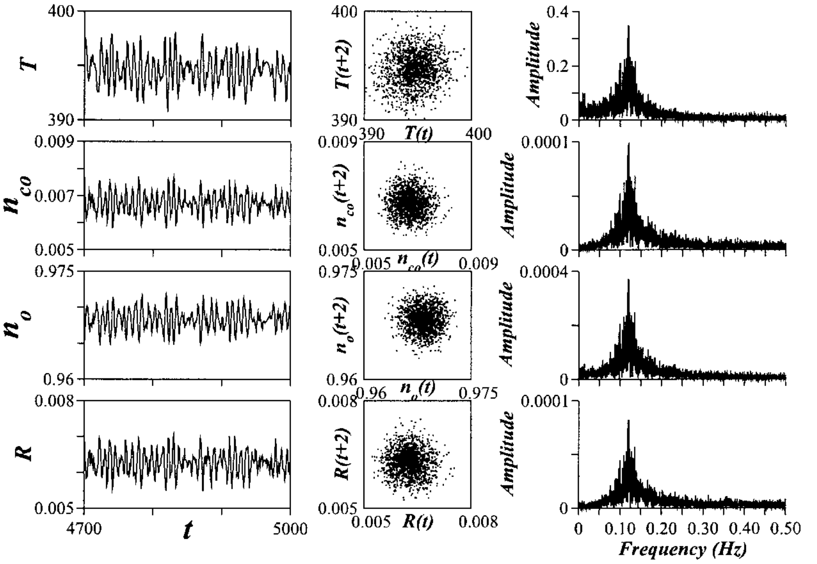

FIG. 3. Time series of the autonomous oscillations (without forcing) of the surface temperature, densities of CO and O, and production of CO_2, for $\gamma=0.05$. These series, obtained by simulations of the CA, correspond to a chaotic region as it can be observed in the scattered filling of the Poincaré maps and the continuous spectra of frequency.

cases. However, for the transitions from chaotic 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 initial random number generator seeds in each simulation, yielding essentially the same results. These results obtained from simulations of our [11,12] CA on a lattice of 256×256 sites and periodical boundary conditions are as follows:

(1) For $0 < \gamma \leq 0.004$ there is a state poisoned by oxygen at $T = T_B$.

(2) For $0.005 \leq \gamma \leq 0.09$ there is an aperiodical regime, where the surface temperature fluctuates around a value greater than the bath temperature, $T > T_B$.

(3) For $0.10 \leq \gamma \leq 0.27$ there is a quasiperiodical regime, where the surface temperature fluctuates around a value greater than the bath temperature, $T > T_B$.

(4) For $\gamma \geq 0.28$ there is a state poisoned by CO at $T = T_B$.

Thus, the CA model is able to describe a variety of behaviors: quasiperiodical and chaotic regimes, and two steady poisoned states.

Typical time series of the autonomous oscillations of the surface temperature, T, coverages of CO, n_{CO}, and O, n_{O}, and production of CO_2, R, corresponding to the quasiperiodical range ($\gamma = 0.25$), are shown in Fig. 2. The quasiperiodical regime is represented qualitatively through the Poincaré maps, where the points are allocated on the same closed curve. Moreover, the Fourier spectrum is discrete and shows two fundamental frequencies: $f_0 = 0.209\,47$ Hz and $f_1 = 0.371\,34$ Hz, because the third peak corresponds to a harmonic of the first fundamental frequency, $2\,f_0 = 0.418\,95$ Hz. Figure 3 is analogous to Fig. 2, but it corresponds to the chaotic range ($\gamma = 0.05$), as the scattered filling of the Poincaré map and the continuous Fourier spectrum demonstrate. For this case, the maximum exponent of Lyapunov is 0.132 571, which corresponds to a chaotic evolution.

III. CONTROL OF CHAOS THROUGH A PERIODICAL PERTURBATION OF T_B

To control chaos a perturbation on T_B is applied, using a sinusoidal function with a single frequency

$$T_B^* = T_B[1 + A \sin(\omega t)], \tag{6}$$

where A is the normalized amplitude and ω is the angular frequency of the perturbation. At the same time, the modulation of the external parameter T_B causes changes in all the active elementary processes (adsorption and reaction).

Systematic variation of A and ω allows one to draw the kinetic phase diagram of the model, showing the different kinds of dynamical states and the bifurcation points. In this paper we want to show the influence of the harmonic variations in T_B on the chaotic state of the reaction, so that a previous knowledge of the range of the parameters where chaotic behavior appears is suitable. Thus, we choose the values of the parameters $\{A_i, E_i, h_i, T_B\}$ given in Sec. II, and then we select the range of variation for A and ω. Following to Kraus *et al.*, [15] we select the frequency of the perturbation [Eq. (6)] that is equal to the natural frequency corresponding to the highest peak of the Fourier spectrum of the chaotic case ($\gamma = 0.05$), $f_0 = 0.119\,38$ Hz, and, consequently, $\omega_0 = 2\,\pi\,f_0 = 0.750\,09$ rad s^{-1}. We fix the values of the rest of the parameters as in the previous section: $A_1 = 5 \times 10^{-2}$, $A_2 = 4 \times 10^5$, $A_3 = 1$, $E_1 = 0$, $E_2/k_B = 6 \times 10^3$ K, $E_3 = 0$, $h_1 = 150$, $h_2 = 300$, $h_3 = 0$, and $T_B = 300$ K, with $\gamma = 0.05$.

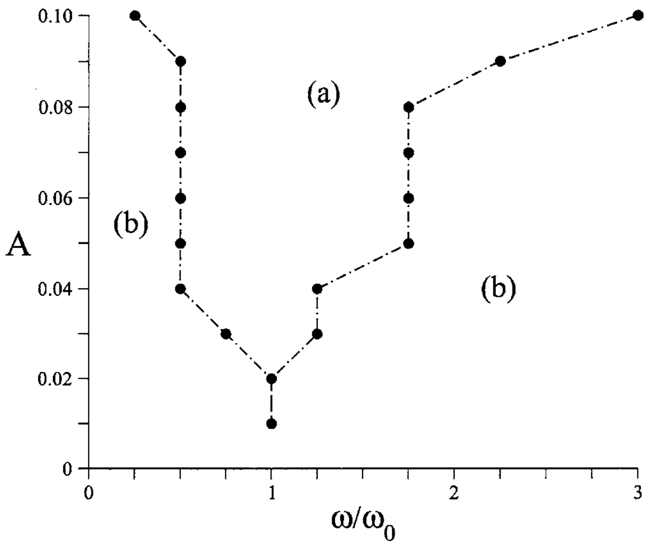

FIG. 4. Kinetic phase diagram obtained through periodical forcing of the environment temperature (T_B) in a model of CA that studies catalytic oxidation of CO allowing the variation of the surface temperature, which differs from that of T_B. The diagram is obtained as a function of the normalized amplitude A and the angular frequency ω of the sinusoidal perturbation on T_B. It can be observed that the technique of periodic forcing converts a chaotic autonomous state found for $\gamma = 0.05$ to period 1 oscillations [regions (a)] for certain values of A and ω, being $\omega_0 = 0.750\,09$ rad s^{-1}. However, there are regions (b) (chaotic oscillations) where a periodical response does not appear when the perturbation is applied. For more details see the text.

The simulation is performed in the usual form described above. For each pair of values of A and ω we have taken 5000 time steps, and we have obtained results for the time evolution of T, n_{CO}, n_{O}, and R, although, for the sake of brevity, we only show the results for T, because those corresponding to the other variables show a similar behavior. We rule out the first 500 points to safely remove the initial transitory regime for all the cases and with the remaining points we calculate the time average of temperature, $\langle T \rangle$, and its fluctuation, θ, so that $T = \langle T \rangle + \theta$. We have carefully analyzed the temperature fluctuation, θ, in order to distinguish chaos from noise and from other behaviors as quasiperiodical and periodical regimes, applying for each time evolution the Fourier transform, the Poincaré map, the maximum Lyapunov exponent, and other tools for the analysis of time series. [16,17]

The kinetic phase diagram of the model is shown in Fig. 4 in terms of the normalized amplitude A and the external frequency ω, both parameters characterizing the study of the dynamical behavior of the perturbed system. Different bands

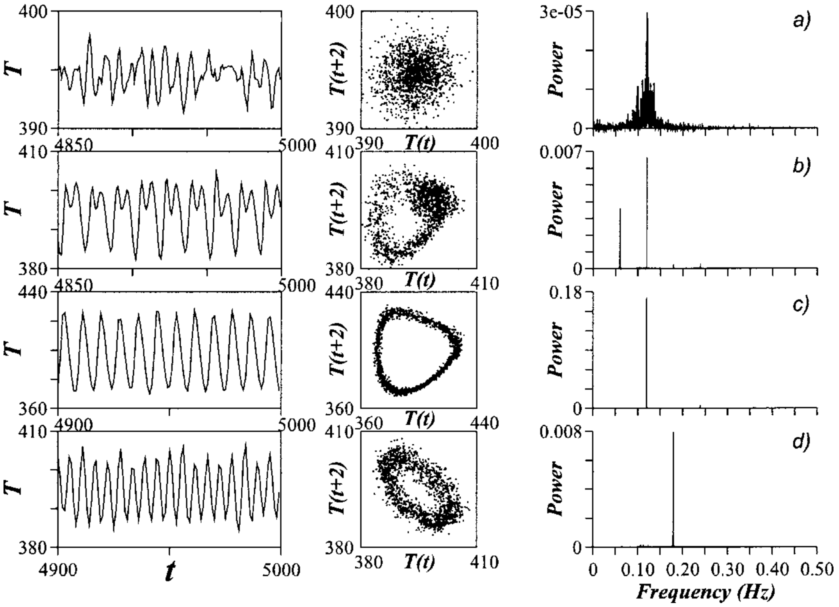

FIG. 5. Typical time series of the surface temperature and its corresponding iterative maps and Fourier spectra for different values of the external frequency. (a) $\omega=0$, autonomous oscillations (without forcing) which depict a chaotic behavior with continuous frequency spectrum. (b) $\omega=0.5\ \omega_0$, train of harmonic waves and stable orbit. The system shows a frequency spectrum discrete with a single fundamental frequency. For (c) $\omega=\omega_0$ and (d) $\omega=1.5\ \omega_0$, the system exhibits stable limit cycles and oscillates with the external frequency imposed. $\gamma=0.05$, $\omega_0=0.750\,09$ rad s^{-1}, and $A=0.08$. The evolutions of the Poincaré maps and the power spectra show that the aperiodical behavior of the system in (a) becomes stable in orbits with period 1 in (b), (c), and (d) when the external frequency increases.

of synchronization or coupling can be observed. A band of synchronization is a region in the phase diagram in which the response is periodical with a period which is a multiple or submultiple of the external frequency. The width of a synchronization band is the range of ω where the response of a system periodically perturbed has a synchronization band for a fixed value of A. It can be observed that when the perturbation applied to the chaotic autonomous region is very weak, for low values of A, a periodical response does not appear. However, for $A=0.01$ (3 K), there is a state in which the system oscillates periodically with a frequency equal to the frequency of the perturbation ($\omega=\omega_0$). We emphasize that this result agrees with the experiments performed by Schwankner *et al.* [18] in the catalytic oxidation of CO on a surface of Pt(100) at low pressure. The periodical modulation of temperature, with a constant amplitude equal to 3 K, caused forced oscillations in the reaction: they observed transitions from autonomous aperiodical oscillations to regular behaviors when the frequency of the perturbation changed. However, this regularity was limited to a certain range of the perturbing frequency. When ω increases, the system trends toward an irregular behavior. According to these authors,

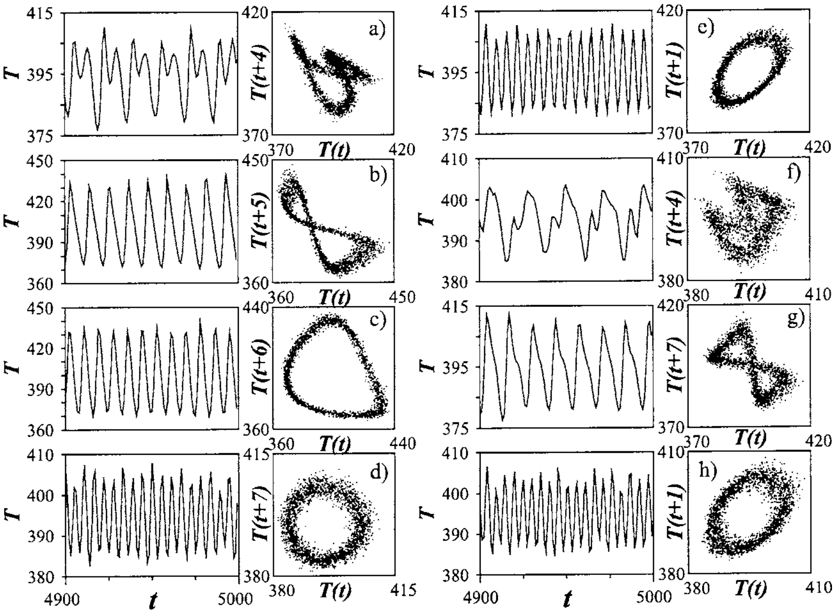

FIG. 6. Time series of the surface temperature and its iterative maps associated for different values of the external frequency. $\gamma=0.05$, $\omega_0=0.750\,09$ rad s^{-1}, and $A=0.10$. (a) $\omega=0.5\ \omega_0$; (b) $\omega=0.75\ \omega_0$; (c) $\omega=\omega_0$; (d) $\omega=1.5\ \omega_0$; (e) $\omega=7\ \omega_0$; (f) $\omega=8\ \omega_0$; (g) $\omega=9\ \omega_0$; (h) $\omega=10\ \omega_0$. The projections of the Poincaré maps show stable orbits at both low and high frequencies.

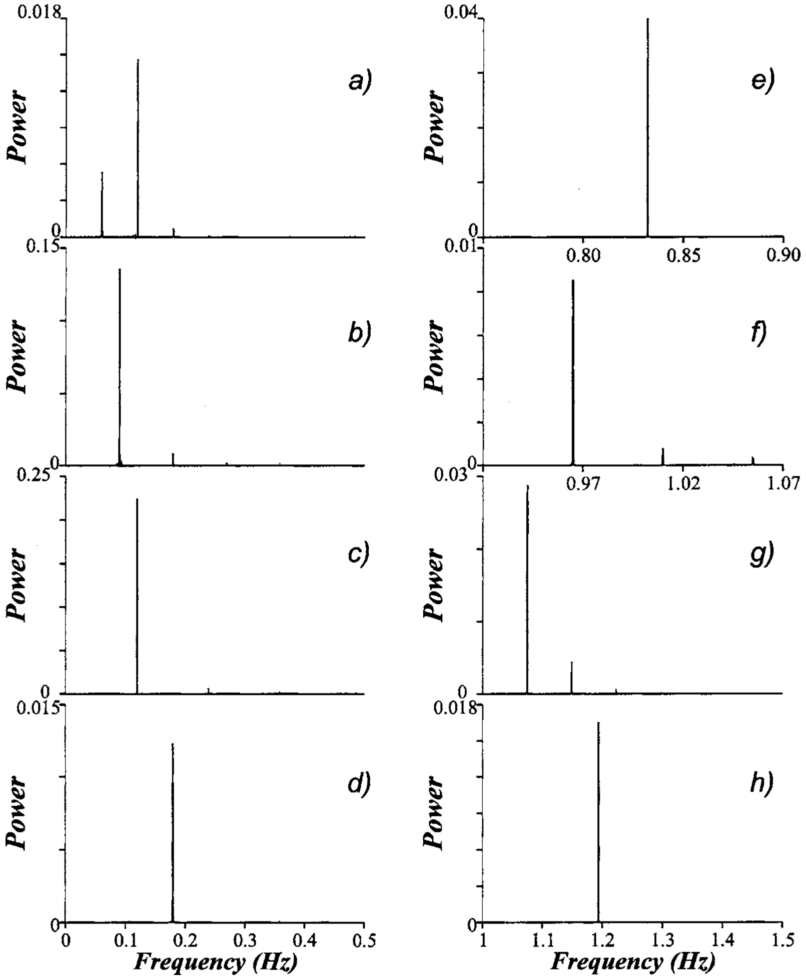

FIG. 7. Power spectra, obtained through the Fourier transform, corresponding to the cases included in Fig. 6 [$\gamma=0.05$, $\omega_0=0.750\,09$ rad s^{-1}, $A=0.10$, and (a) $\omega=0.5\ \omega_0$; (b) $\omega=0.75\ \omega_0$; (c) $\omega=\omega_0$; (d) $\omega=1.5\ \omega_0$; (e) $\omega=7\ \omega_0$; (f) $\omega=8\ \omega_0$; (g) $\omega=9\ \omega0$; (h) $\omega=10\ \omega_0$]. The system shows a periodical behavior for all cases: the Fourier spectrum is discrete with only a fundamental frequency, although its harmonics of less intensity can be observed as well.

these facts agreed qualitatively with the guidelines of the general experience in nonlinear forced oscillations.

As the perturbing amplitude increases, the simulations of the CA model show that the range of external frequency resonant with the dynamical system increases as well. So, oscillatory states with period 1 with frequency equal to the external frequency can appear for intermediate values of A. Finally, if A is great, the response of the system is always synchronized for any value of ω. In order to analyze the way in which the chaotic behavior of the reaction changes when the external modulation varies, we have chosen a control band in the phase diagram with A fixed, now ω being the only control parameter.

Some typical time series of the surface temperature, T, and the corresponding Poincaré maps and the Fourier spectra, for different values of the external frequency, are shown in Fig. 5, for $\gamma=0.05$, $\omega_0=0.750\,09$ rad s^{-1} and $A=0.08$. For (a) $\omega=0$, the autonomous oscillations (without forcing) show chaotic behavior: the trajectories are erratic and the frequency spectrum is continuous. For (b) $\omega=0.5\ \omega_0$, the orbit becomes stable and the trajectories are projected on the same closed curve. Characteristic peaks are observed when the frequency of the external perturbation is resonant with the dynamical system; the most prominent peak corresponds to the frequency 0.119 38 Hz, and its harmonic 0.059 57 Hz can be observed as well. For this case the system oscillates periodically with a frequency which is twice the frequency imposed. For (c) $\omega=\omega_0$, the projected orbit corresponds to a limit cycle, its fundamental frequency being 0.119 38 Hz. Finally, for (d) $\omega=1.5\ \omega_0$, the resonant peak appears when the frequency is 0.178 96 Hz. For the cases (c) and (d) the system oscillates with the external frequency. The iterative maps and the power spectra show that the chaotic behavior of the system in (a) becomes stable into orbits P1 in (b), (c), and (d) when the external frequency increases. If A is great, for any value of ω, the response of the system is always synchronized and the system responds with the frequency of the external perturbation or a multiple of it. This result is shown in Figs. 6 and 7. In Fig. 6 some time series of the surface temperature, T, and its corresponding Poincaré maps (for different time delays) are shown, for $\gamma=0.05$, $\omega_0=0.750\,09$ rad s^{-1}, $A=0.10$, and (a) $\omega=0.5\ \omega_0$, (b) $\omega=0.75\ \omega_0$, (c) $\omega=\omega_0$, (d) $\omega=1.5\ \omega_0$, (e) $\omega=7\ \omega_0$, (f) $\omega=8\ \omega_0$, (g) $\omega=9\ \omega_0$, and (h) $\omega=10\ \omega_0$. As for both low and high frequencies, the projections of the iterative maps show stable orbits. The different power spectra, obtained through the usual Fourier transform, corresponding to the cases included in Fig. 6, are shown in Fig. 7. Characteristic peaks are observed when ω is resonant with the dynamical system. Resonant peaks appear in the following situations: (a) For $\omega/\omega_0=0.5$, peaks are observed at 0.059 57 Hz, 0.119 38 Hz, 0.178 96 Hz, and 0.238 77 Hz. The most prominent peak is at 0.119 38 Hz, which corresponds to a subharmonic, because this frequency is twice the frequency of the perturbation. For (b) $\omega/\omega_0=0.75$, the most prominent peak is at 0.0896 Hz, and its harmonics are 0.178 96 Hz and 0.268 55 Hz. For (c) $\omega/\omega_0=1$, the resonant peak appears at 0.119 38 Hz and its harmonic is 0.238 77 Hz. For (d) $\omega/\omega_0=1.5$, the peak is observed at the external frequency 0.178 96 Hz. The cases (e) $\omega=7\ \omega_0$, (f) $\omega=8\ \omega_0$, (g) $\omega=9\ \omega_0$, and (h) $\omega=10\ \omega_0$ are similar to (d), and the system oscillates with the imposed frequency: (e) 0.835 66 Hz, (f) 0.955 04 Hz, (g) 1.074 42 Hz, and (h) 1.193 85 Hz. Thus, for $A=0.10$, the frequency of the system is twice [case (a)] or equal to (all the remaining cases) the frequency of the perturbation. For this band the coupling is a phenomenon of resonance and causes a response greater than for other bands with less amplitude. The prominent peaks appear when there is resonance between the autonomous chaotic system and the perturbation. Similar results to those obtained for the band $A=0.10$ are obtained for the bands $A=0.11$, 0.12, 0.15, 0.20, and 0.50. This fact allows us to affirm that as of $A=0.10$, the system oscillates periodically because the response of the system is always synchronized for the range of the external frequency tested.

In a previous paper [19], to control chaos, the frequency factor A_2 of the oxygen adsorption rate [Eq. (2)] was perturbed periodically with a sinusoidal function with a single frequency. The phase diagram there obtained showed synchronization bands from high amplitudes ($A\geq 0.20$); these bands became narrower as the perturbing frequency increased. This is attributed to the fact that temperature modulation simultaneously causes great changes in all the active elementary processes, which prevents a clear interpretation of the response of the system, while the variation of the oxygen adsorption rate affects mainly this species. [18] Thus, a little change in room temperature causes a greater change in the elementary processes than great changes in the oxygen adsorption rate, exhibiting, therefore, wide ranges of coupling for little amplitudes. However, the periodical modulations of A_2 and T_B lead qualitatively to the same phenomenon: the external forcing method is capable to control chaos converting it to periodical evolution, a perturbing harmonic function with a single frequency being enough to transform a chaotic state in states with periodicity 1.

IV. CONCLUSIONS

We have dealt here with a model of CA to simulate the oscillatory behavior of the reaction of CO and O on metallic surfaces. For this purpose, we extended the Mai-Niessen steady model [4] including the surface temperature as a dynamic variable. The nonlinear dependence of the rates on the temperature given by the Arrhenius law in the CA model gives rise to quasiperiodical and chaotic regimes, where the surface temperature fluctuates around a temperature greater than the environment one. For the recognition of chaos we have proceeded in the usual way, studying the time series obtained from the simulations of the CA, through the building of recurrence graphics, Poincaré maps, Fourier transform and other typical quantities of the nonlinear analysis such as the space-time entropy and the maximum Lyapunov exponent.

The appearance of chaotic states in the CA model lead us to attempt its control by means of its conversion to periodic states, applying the periodical forcing method. In contrast to other chaos control methods such as that of Pyragas [15], which requires the redefinition of the feedback constant of the system, the simplicity of the periodical forcing method is based on the resonance phenomenon, the amplitude and the frequency of the external perturbation being the parameters characterizing the dynamic study of the perturbed system.

In this paper, in the range of parameters in which the autonomous chaotic behavior exists, we perturb the environment temperature through a sinusoidal function with a single frequency, obtaining a kinetic phase diagram of the model in terms of the normalized amplitude and the angular frequency of the external perturbation (Fig. 4). We show that if the normalized amplitude is greater than a certain value, the system exhibits oscillations of period 1 with the frequency of the external perturbation or a multiple of it. As the normalized amplitude decreases, the synchronization band is narrower, that is to say, for a given value of the perturbing amplitude the range of external frequencies that are synchronized with the system is narrower. These results agree qualitatively with experiments and theoretical studies of forced nonlinear oscillations in the catalytic oxidation of CO. Thus, the strategy of control through periodical forcing, for relatively little variations of the bath temperature, is able to remove the chaotic dynamics through stabilization of periodical solutions, a perturbing harmonic function with a single frequency being enough to transform chaotic states in periodical ones with periodicity 1. Besides the interesting character of this result from a theoretical viewpoint, it also has the advantage in the practical applications in heterogeneous catalysis of removing the chaotic evolution, which is erratic and unpredictable, and is usually considered undesirable. Finally the study realized reveals, on the one hand, the ability of the CA to model this kind of reactions in an easy way and to gain insight in essential aspects of the steady and oscillatory behavior of the oxidation of CO and, on the other, the simplicity of the periodical forcing method makes this a strategy that can be used to clarify the mechanisms of reactions and to obtain data on reaction rates for both steady and oscillatory kinetics.

ACKNOWLEDGMENTS

This work is partially financed by the Spanish Government (Project No. BFM2003-03986/FISI), the European Fund for Regional Development, and the Junta de Andalucía (FQM-122).

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