

## Bistability and oscillations in a surface reaction model

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Multiple stationary states and oscillations of temperature and concentrations are observed in a kinetic surface reaction model, based on the oxidation of carbon monoxide on a catalyst surface. Equations governing the reaction are obtained by using a mean-field approximation type. Bistability and sustained oscillations are observed within certain limits of the temperature relaxation parameter and operating condition.

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### I. INTRODUCTION

Surface reactions, when operating as open systems, behave as nonequilibrium systems [1]. They show kinetic phase transitions, bistability, and associated hysteresis, oscillations, transition to chaos, etc. Most oxidation reactions catalyzed by metals of the platinum or palladium groups exhibit such properties, the catalyzed oxidation of carbon monoxide being a good example of these types of behavior. This is the most thoroughly studied surface reaction, as demonstrated by the great number of experimental and theoretical studies reported in the literature [2–6].

An extensive variety of kinetic models involving nonlinearities of different natures have been proposed to simulate multiple steady states and oscillations in catalytic carbon monoxide reactions. Thus, models where, because of reaction heats, the catalytic surface can maintain a different temperature from that of its surroundings and temperature oscillations can originate jointly with concentration oscillations have been considered [7–9]. Temperature fluctuations give rise to a strong nonlinearity of kinetic equations owing to the Arrhenius law.

Lagos, Sales, and Suhl [7] proposed a model to analyze the behavior of the reaction  $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$  over platinum. Their model was constructed on the basis of the experimental results reported by Dauchot and Van Cakenberghe [10], which anticipated that the key to the occurrence of oscillations turns out to be the finite time required for the decay of temperature fluctuations of the platinum surface. The mechanism proposed by these experimenters is the following: Adsorption of  $\text{O}_2$  is favored over that of CO by an increase in temperature of the catalyst. Thus, starting from the hot surface,  $\text{O}_2$  has been mostly adsorbed. As the system cools down (its surroundings are at a constant and different temperature), CO is progressively adsorbed and the reaction proceeds rapidly. The CO is eliminated by the Langmuir-Hinshelwood mechanism and the hot surface resulting from that exothermic reaction is again covered primarily and rapidly with  $\text{O}_2$ .

From experimental results it is known that (a) the adsorption of CO on the surface is unactivated; (b) the adsorption of  $\text{O}_2$  on the surface is activated with an activa-

tion energy of about 4.5 kcal/mole; (c) for temperatures of 300–550 K, the rate of desorption of CO from the surface is much less than the rate of removal of CO from the surface via the Langmuir-Hinshelwood reaction, that is, long before the CO desorbs it reacts with the O on the surface to form  $\text{CO}_2$ ; (d) for temperatures below 550 K, the desorption of  $\text{O}_2$  is slower and can be ignored; (e) for temperatures between 300 and 400 K, the reaction between the O and CO on the surface is weakly activated and can be neglected; (f)  $\text{CO}_2$  formed on the surface is weakly bound.

On the basis of mean-field theory, Lagos, Sales, and Suhl [7] obtained the kinetic equations by using the singlet closure approximation (SCA), or site approximation, and assuming that the surface is a square lattice. They obtained multiplicity of stable stationary states and oscillations.

This known model was extended by Lemos and Córdoba [11] in order to consider other features of the problem. Specifically, they analyzed the influence that the system dimension and the kind of closure approximation used to obtain the kinetic equations has on the existence of multiplicity and oscillations. Also, in contrast to the model of Lagos, Sales, and Suhl [7], in their model they have considered the role played by desorption of reactants. They conclude that the nonlinearity introduced in the model formulated to study the catalyzed oxidation of carbon monoxide does not give rise to multiplicity of stable steady states or oscillations in one-dimensional systems when the doublet closure approximation (DCA), or pair approximation, is applied, but does when the system is two dimensional. As in other cases of equilibrium and nonequilibrium phase transitions, it is made clear that these take place in two-dimensional systems but not in one-dimensional ones and, therefore, the transition appearing when the SCA is applied to a one-dimensional system is spurious and a consequence of the approximation applied.

Based on a model proposed by Ziff, Gulari, and Barshad [3], Luque [12] has studied this reaction deriving the kinetic equations by starting from a master equation following the generalized model of Glauber-Ising. Since the distribution of adsorbed particles on the surface can affect the transition probabilities in the adsorption and desorption processes, the spatial correlations were con-

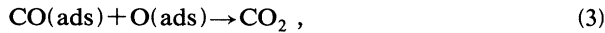
sidered and clusters that involved up to eight sites were introduced. A set of five nonlinear kinetic equations was obtained for the densities of CO ( $n_{\text{CO}}$ ) and atoms O ( $n_{\text{O}}$ ), and pairs CO—CO ( $n_{\text{CO—CO}}$ ), CO—O ( $n_{\text{CO—O}}$ ), and O—O ( $n_{\text{O—O}}$ ) considering a doublet closure approximation. In addition to three zones obtained by Ziff, Gulari, and Barshad [3] [(a) the catalyst is poisoned by O<sub>2</sub>, (b) there is a reactive steady state where CO<sub>2</sub> molecules are produced, and (c) the catalyst is poisoned by CO], a bistability zone was found: one state a reactive stable state producing CO<sub>2</sub> and another in which the catalyst is poisoned by CO; depending on initial conditions, the reaction will evolve toward one of the two stable stationary states.

In order to study what effects take place in the reaction when the temperature of the catalyst is changing, the former model [12] was chosen, introducing another equation where these changes are considered.

In the next section, the Luque model is analyzed and extended by adding an equation for the rate of change of the surface temperature. The results and conclusions are described in the last section.

## II. THE MODEL FOR A SQUARE LATTICE USING A DOUBLET CLOSURE APPROXIMATION

Model [12] assumes that the reaction takes place according to three kinetic mechanisms:



where (ads) indicates that the molecule is adsorbed on the surface, following the Langmuir-Hinshelwood model.

The surface of the catalyst is a square two-dimensional lattice of active sites and the assumption is that the molecules of carbon monoxide (CO) and the oxygen atoms (O) both occupy single sites on the lattice. The oxygen and carbon monoxide molecules collide randomly on the surface and when there is a site available they are adsorbed. Two adjacent sites are needed for the oxygen molecule to be adsorbed. Upon adsorption, the O<sub>2</sub> dissociates into two O atoms, each residing on a separate surface site. When a molecule adsorbs on the surface, it becomes fixed, so that superficial diffusion is ignored in this model.

A carbon monoxide molecule CO adsorbed on the surface can interact with the four nearest-neighbor particles, leaving the surface when it finds a neighbor oxygen atom to join, forming a carbon dioxide molecule. An oxygen molecule O<sub>2</sub> adsorbed on the surface can interact with its six nearest neighbors, one oxygen atom leaving the surface when meeting a neighbor carbon monoxide molecule to form a carbon dioxide molecule.

The master equation, containing the three elemental mechanisms cited above, is formulated, with  $W_i$  the transition probability for each of them ( $i=1$ , adsorption of CO;  $i=2$ , adsorption of O<sub>2</sub>;  $i=3$ , desorption of CO<sub>2</sub>). The transition probabilities are chosen in the Arrhenius form:

$$W_i = A_i \exp \left[ -\frac{E_i}{kT} \right], \quad (4)$$

where  $A_i$  are frequency factors,  $k$  is the Boltzmann constant,  $T$  denotes the temperature of the surface, and  $E_i$  are activation energies.

Kinetic equations have been obtained by applying a closure approximation consisting of closing the hierarchy of kinetic equations at the level of doublets (DCA) [11,12]. In a DCA the state of the surface is determined, giving the density of single particles  $n_i$  and the density of pairs,  $n_{ij}^x$  and  $n_{ij}^y$ , where  $i, j = \text{CO}, \text{O},$  and  $V$  (vacancy), and  $x$  ( $y$ ) indicates that the pair is situated on the  $x$  axis ( $y$  axis). By dependence relationship among the variables  $n_i$ ,  $n_{ij}^x$ , and  $n_{ij}^y$ , and for consideration of symmetry, since there are no preferred sites on the  $x$  and  $y$  axes,  $n_{ij}^x = n_{ij}^y$ , the number of independent variables can be reduced to  $n_{\text{CO}}, n_{\text{O}}, n_{\text{CO—CO}}^x, n_{\text{CO—O}}^x,$  and  $n_{\text{O—O}}^x$ .

The evolution equations are

$$\frac{dn_{\text{CO}}}{dt} = n_5[V] - 4n_8[\text{CO—O}], \quad (5)$$

$$\frac{dn_{\text{O}}}{dt} = 4n_8[V—V] - 4n_8[\text{CO—O}], \quad (6)$$

$$\frac{dn_{\text{CO—CO}}^x}{dt} = 2n_5[\text{CO—V}] - 6n_8[\text{CO—CO—O}], \quad (7)$$

$$\begin{aligned} \frac{dn_{\text{CO—O}}^x}{dt} = & n_5[\text{O—V}] - 3n_8[\text{CO—V—V}] \\ & - n_8[\text{CO—O}] - 3n_8[\text{O—CO—O}] \\ & - 3n_8[\text{CO—O—CO}], \end{aligned} \quad (8)$$

$$\begin{aligned} \frac{dn_{\text{O—O}}^x}{dt} = & n_8[V—V] + 6n_8[\text{O—V—V}] \\ & - 6n_8[\text{O—O—CO}], \end{aligned} \quad (9)$$

where

$$n_5[V] = n \begin{bmatrix} & \times & \\ \times & V & \times \\ & \times & \end{bmatrix} W_1, \quad (10)$$

$$n_5[z—V] = n \begin{bmatrix} & \times & \\ z & V & \times \\ & \times & \end{bmatrix} W_1, \quad (11)$$

$$n_8[r—s] = n \begin{bmatrix} & \times & \times & \\ \times & r & s & \times \\ & \times & \times & \end{bmatrix} W_i, \quad (12)$$

$$n_8[z—r—s] = n \begin{bmatrix} & \times & \times & \\ z & r & s & \times \\ & \times & \times & \end{bmatrix} W_i. \quad (13)$$

We use

$$n \begin{bmatrix} & \times & \\ \times & V & \times \\ & \times & \end{bmatrix}$$

to denote the density of cluster of five sites which have in the center a vacant site and

$$n \begin{bmatrix} & \times & \times \\ \times & r & s & \times \\ & \times & \times & \end{bmatrix}$$

to denote the density of cluster of eight sites whose center can be occupied by CO—O, O—CO, or V—V.  $\times$  represents indistinctly CO, O, and vacancy. One  $\times$  substituted by  $z$  means that this site can only be occupied by the monomer indicated: CO or O.  $W_i$  in (12) and (13) is  $W_2$  for  $r-s = V-V$  and  $W_3$  for  $r-s = \text{CO—O}, \text{O—CO}$ . We assume the closure approximation

$$n \begin{bmatrix} 1 \\ 2 & V & 4 \\ 3 \end{bmatrix} = (n_{V-1}n_{V-2}n_{V-3}n_{V-4})/n_V^3 \quad (14)$$

and

$$n \begin{bmatrix} 1 & 6 \\ 2 & r & s & 5 \\ 3 & 4 \end{bmatrix} = \frac{(n_{r-1}n_{r-2}n_{r-3}n_{r-s}n_{s-4}n_{s-5}n_{s-6})}{(n_r^3n_s^3)}, \quad (15)$$

where 1, 2, 3, 4, 5, and 6 can be indistinctly occupied by CO, O, and V, and  $n_i$  and  $n_{i-j}$  are the density of monomers and pairs of type  $i$  and  $i-j$  on the lattice. In Ref. [12] there is a detailed explanation of how kinetic equations describing the evolution of the reaction are obtained.

Thus, in this model, the spatial correlations were considered and larger clusters that involve five and eight sites on the surface were introduced.

Now, and in order to study the oscillatory behavior of the reaction, the evolution equations must be supplemented by an equation for the rate of change of the surface temperature:

$$C \frac{dT}{dt} = -L(T - T_B) + \sum_{i=1}^3 \Delta H_i W_i, \quad (16)$$

where  $C$  is the heat capacity of the system,  $L/C$  ( $L$  is approximately equal to thermal conductivity times a geometric factor) is the relaxation rate of  $T$  to  $T_B$ ,  $T_B$  being room temperature, and  $\Delta H_i$  are the reaction heats of the processes (1), (2), and (3), including a suitable geometric factor.

Equation (16) can be written

$$\frac{dT}{dt} = -\gamma(T - T_B) + h_1 n_5 [V] + 2h_2 n_8 [V-V] + 4h_3 n_8 [\text{CO—O}], \quad (17)$$

where  $\gamma = L/C$  and  $h_i = \Delta H_i/C$ .

Kinetic equations can give rise to oscillatory states for certain values of the ten parameters  $\Gamma = \{A_i, E_i, h_i, \gamma\}$ , room temperature being at  $T_B = 300$  K.

### III. RESULTS

With the purpose of studying the occurrence of oscillations in this reaction, the set of six nonlinear kinetic

equations are considered, each of them equal to zero. Thus, we have a system of nonlinear equations that are solved numerically with the Newton-Raphson method.

Initially, the problem was complicated, since describing the reaction requires many parameters. Our kinetic model was constructed on the basis of the present experimental understanding of this particular reaction, and wherever possible, the values for the parameters reported in the literature were used, adapting them to those of our model.

First, and according to experimental results, we assume that as 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  $\text{O}_2$  is the only activated process. We make a minor simplification considering that the heat reaction for the adsorption of  $\text{O}_2$  is twice the value of that of the CO and the heat reaction for  $\text{CO}_2$  is negligible and so  $h_2 = 2h_1$  and  $h_3 = 0$ . Likewise, we include parameter  $A_3$  in the time in kinetic equations (5)–(9) and (17) and operate with a scaled time; therefore  $A_1 = A_1/A_3$ ,  $A_2 = A_2/A_3$  and  $A_3 = 1$ . Finally, and because the occurrence of oscillations depends essentially on the temperature relaxation parameter ( $\gamma$ ), we have analyzed here the case where  $\gamma$  varies, keeping all others parameters fixed.

For values  $A_1 = 0.05$ ,  $A_2 = 400\,000$ ,  $A_3 = 1$ ,  $E_1 = 0$ ,  $E_2 = 6000$ ,  $E_3 = 0$ ,  $h_1 = 150$ ,  $h_2 = 300$ ,  $h_3 = 0$ , and all values of  $\gamma$ , there is a state corresponding to complete coverage with CO at room temperature, which is a stable node. Besides this stable node, a new solution which is either a stable node or a focus is found when the values of  $\gamma$  are in the range  $0.03 \leq \gamma \leq 0.15$ . Outside of this interval, the new state vanishes. This new state can be either an oscillatory state in the range  $0.10 \leq \gamma \leq 0.15$  or a stable node for  $0.03 \leq \gamma \leq 0.09$ , corresponding to a reactive steady state producing  $\text{CO}_2$  at a temperature greater than room temperature.

In Fig. 1 the oscillations of temperature and concentration of CO-adsorbed species, together with the associated

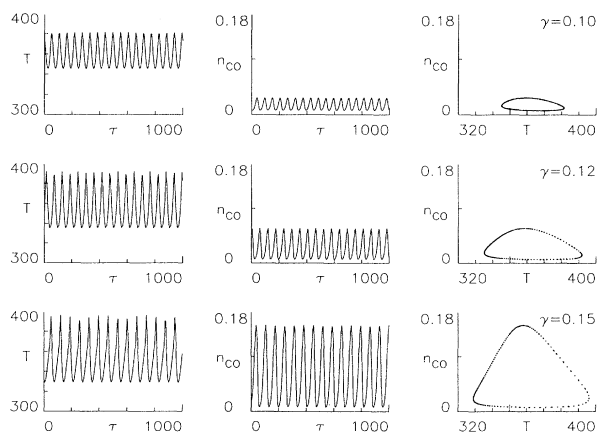


FIG. 1. Development of the oscillations of temperature (in K) and concentration of adsorbed CO, and the associated limit cycles drawn on the  $T$ - $n_{\text{CO}}$  phase plane for different values of  $\gamma$ .

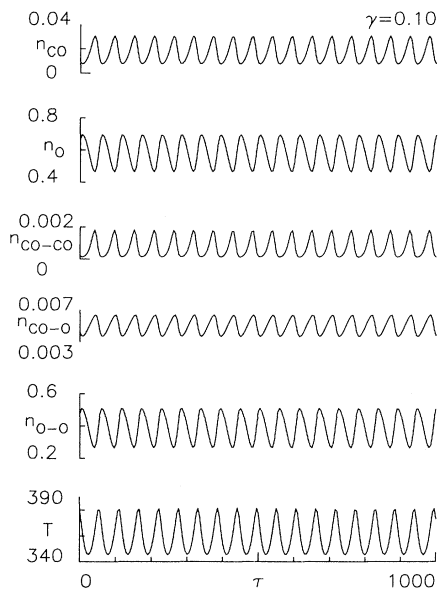


FIG. 2. Oscillations of concentrations and temperature (in K) for  $\gamma=0.10$ .

limited cycles drawn on the  $T-n_{CO}$  phase plane, are shown for different values of  $\gamma$ . Outside of the interval  $0.10 \leq \gamma \leq 0.15$ , oscillations are not found. As can be seen, the oscillation amplitude and the size of the limit cycle increase as  $\gamma$  increases until, at  $\gamma=0.16$ , the oscillatory state disappears. Thus, for  $\gamma \geq 0.16$ , the only stable solution corresponds to the catalyst poisoned by CO at room temperature.

Oscillations of the catalyst temperature and coverage fractions  $n_{CO}$ ,  $n_O$ ,  $n_{CO-CO}$ ,  $n_{CO-O}$ , and  $n_{O-O}$  for  $\gamma=0.10$  are shown in Fig. 2. Dissociative  $O_2$  adsorption is favored over that of CO by increasing the temperature of the catalyst.

Figure 3 corresponds to the projections on the  $T-n_{CO}$ ,  $T-n_O$ , and  $n_{CO}-n_O$  planes of limit cycle obtained for  $\gamma=0.10$ . The limit cycle in the  $n_{CO}-n_O$  phase plane is similar to that obtained by Imbihl *et al.* [4] when a surface phase-transition model was analyzed, which had been proposed to explain kinetic oscillations in the catalytic CO oxidation on Pt(100). This model was based on experimental investigations on well defined Pt(100) surfaces also carried out by these researchers [4].

On the other hand, for the range  $0.03 \leq \gamma \leq 0.09$ , the new state is a stable node corresponding to a decreasing adsorption of CO favored by increasing temperature and adsorption of  $O_2$ . Thus, Fig. 4(a) shows the stable node obtained for  $\gamma=0.08$ . The temperature of the catalyst and the coverage fractions are:  $T=364$  K,  $n_{CO}=0.011$ ,  $n_O=0.646$ ,  $n_{CO-CO}=0.0003$ ,  $n_{CO-O}=0.004$ ,  $n_{O-O}=0.456$ . This state, and the previous transient oscillatory state, can exist together with the stable state of complete CO coverage. However, outside of the interval  $0.03 \leq \gamma \leq 0.15$ , this new state disappears. Our results are

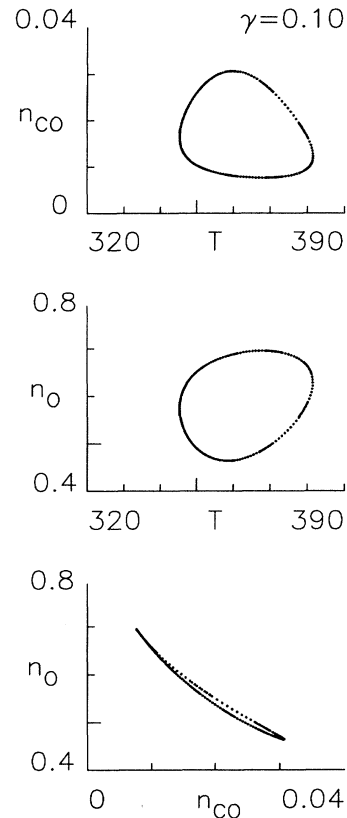


FIG. 3. Projections on different phase planes of the limit cycle obtained for  $\gamma=0.10$ . Temperature  $T$  is in Kelvin.

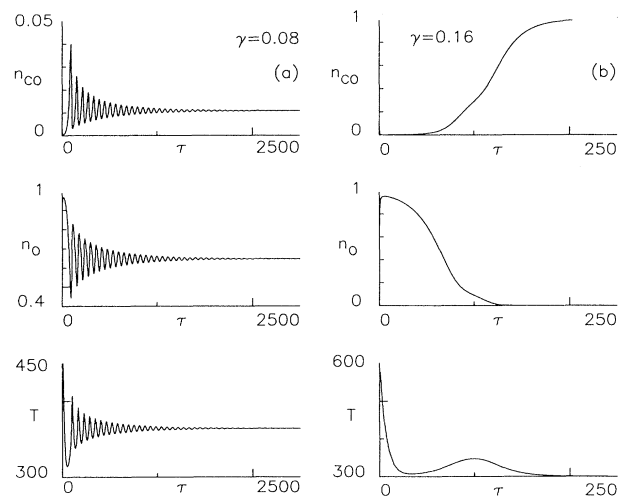


FIG. 4. (a) Stable stationary state obtained for  $\gamma=0.08$ , with decrease in adsorption of CO and increase in temperature (in K) of the surface, favoring adsorption of  $O_2$  and producing  $CO_2$ . (b) Stable stationary state for  $\gamma=0.16$ , the only state corresponding to the poisoning of the surface by CO at room temperature (in K).

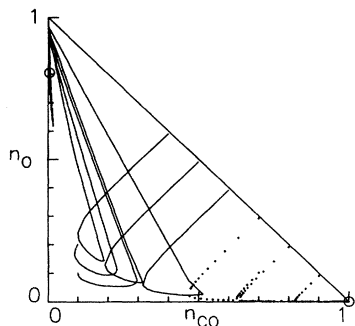


FIG. 5. Projection on the  $n_{\text{CO}}-n_{\text{O}}$  phase plane of several trajectories obtained with different initial conditions, for  $\gamma=0.04$ . Orbits do not cross themselves; the apparent crossing is due to the projection on the plane.  $\circ$  denotes stable stationary solutions.

in qualitative agreement with those obtained by others authors (see Ref. [13], where the author presents in Chapter 10 some works on the catalytic oxidation of carbon monoxide, summarizing their more important aspects). In Fig. 4(b), for  $\gamma=0.16$ , it can be seen that still starting from the hot surface, the catalyst is covered rapidly with CO, thus producing poisoning of the surface by this reactant.

Figure 5, for  $\gamma=0.04$ , shows the projection on the  $n_{\text{CO}}-n_{\text{O}}$  phase plane of some trajectories obtained with different initial conditions for  $n_{\text{CO}}$  and  $n_{\text{O}}$ . Initial values for the pairs are chosen, starting from random distribution of monomers on the surface; thus,  $n_{\text{CO-CO}}=n_{\text{CO}}n_{\text{CO}}$ ,  $n_{\text{CO-O}}=n_{\text{CO}}n_{\text{O}}$ , and  $n_{\text{O-O}}=n_{\text{O}}n_{\text{O}}$ . The initial temperature of the system is  $T_B$ . The apparent cross-

ing of the trajectories is due to the projection on the  $n_{\text{CO}}-n_{\text{O}}$  plane and orbits do not cross themselves. This figure represents a bistability zone, where  $\circ$  denotes stable nodes. The phase space can be shown to divide into two different attraction zones, each of the trajectories converging into one of the two stable states of the system. One is a reactive stable state with  $T=372$  K,  $n_{\text{CO}}=0.004$ ,  $n_{\text{O}}=0.805$ ,  $n_{\text{CO-CO}}=0.00005$ ,  $n_{\text{CO-O}}=0.002$ , and  $n_{\text{O-O}}=0.674$ . In the other stable node the catalyst is poisoned by CO at room temperature.

Summarizing, the nonlinearity introduced in the model gives rise to multiple stationary states and oscillations, the kinetic phase transitions taking place being (a) 1 stable node  $\Rightarrow$  2 stable nodes; (b) 1 stable node  $\Rightarrow$  1 stable node and 1 limit cycle, and (c) 2 stable nodes  $\Rightarrow$  1 stable node and 1 limit cycle. There is a stable node corresponding to complete coverage with CO at room temperature. The other stable node and oscillatory state appear only for certain values of the temperature relaxation parameter. In this new state, the temperature of the surface is or fluctuates around a temperature greater than that of room temperature, thus favoring the adsorption of  $\text{O}_2$  and decreasing the adsorption of CO. So, in this surface reaction model the sustained temporal oscillation of the reaction products is accompanied by oscillation of the catalyst temperature. As in other models, the relaxation rate of the surface temperature plays an important role in the onset of oscillations.

#### ACKNOWLEDGMENTS

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