External noise-induced phenomena in CO oxidation on single crystal surfaces

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The influence of external noise on minimalistic models for the catalytic CO oxidation on Ir(111) and Pt(111) is studied by means of the adiabatic elimination technique. Two models, which reproduce the bistable behavior usually observed in CO oxidation on Pt group metal surfaces, are analyzed. The noise is superposed on the fraction of CO in the constant gas flow directed at the surfaces and the resulting stochastic systems are reduced after the adiabatic elimination of oxygen coverage. This reduction allows us to analyze theoretically the interplay between external noise and the kinetic bistability of CO oxidation. We report the phenomena of noise-induced shifts of steady states and noise-induced jumps between stable steady states. We also present evidence for noise-induced transitions from mono- to bistability. The theoretical results are compared with simulations of the original two-variable stochastic reaction systems. © *2009 American Institute of Physics.*
[DOI: 10.1063/1.3096989]

I. INTRODUCTION

Stochastic fluctuations or noise in complex dynamical systems with strong nonlinearities give rise to unexpected and new ordering phenomena.[1] Chemical reactions on solid surfaces exhibit nonlinear behavior, such as bistability, self-sustained kinetic oscillations, chaos, and spatiotemporal patterns.[2] For this reason, understanding the influence of noise on the complex behavior of catalytic surface reactions has become a challenge in recent years. In general, the effects of internal noise (due to finite-size effects) and external noise (imposed on the external control parameters) have been considered separately. In this paper we present a theoretical study of external noise imposed on the catalytic CO oxidation on Ir(111) and Pt(111).

The experimental characterization of noise-induced effects in surface reactions is rather difficult and, therefore, very few experiments are reported in the literature. In particular, the interplay between internal noise and catalytic surface reactions has scarcely been studied experimentally because well defined experiments are inherently difficult.[3] In one of the few experimental works available, the role of internal noise on CO oxidation on nanofacets of a Pt field emitter tip has been studied with field electron microscopy.[4] It was shown that noise induces transitions between the two kinetic stationary states that coexist in the bistable range. In another set of experiments,[5] by varying the diameter of Pd nanoparticles, it was demonstrated using molecular beams that bistability in catalytic CO oxidation vanishes below a critical particle size. Kinetic Monte Carlo simulations, mean-field stochastic simulations, and analytical solutions of a mean-field master equation have been implemented to clarify those results.[6–9] It was also proposed that such internal noise may not only arise on nanoscale surfaces but also on macro-

scopic surface planes if we choose conditions, which restrict the diffusion length of adsorbed particles such that again the number of reacting particles becomes sufficiently small. Random patterns ("raindrop patterns") observed in catalytic CO oxidation on Pt(110) at high pressure were interpreted in this way.[10–12]

The effects induced by external noise on surface reactions have also been experimentally explored. Several years ago, the NO+CO catalytic reduction system on Pt(100) was experimentally studied under external random perturbations.[13] More recently, the influence of external noise on catalytic surface reactions has been systematically studied in the catalytic CO oxidation on Ir(111). The external noise was imposed in the CO fraction of the constant total reactant gas flux and on the temperature of the catalyst.[14,15] In the case of noise on the gas flux a shift of the stationary reaction rate depending of the noise intensity and a noise-induced switching between the two stable branches of the bistable region were found.[16] The emergence of spatiotemporal structures in the CO oxidation on Pt(110) when global noise is introduced externally has also been experimentally studied. In this system, it was shown that noise behaves as an overall coordinating factor that gives a certain spatial coherence. In this way, chemical turbulence can be suppressed.[17,18] The phenomenon of stochastic resonance has been also reported theoretically in models of catalytic CO oxidation and catalytic NO reduction on Pt surfaces.[19–21] Nevertheless, there are no experimental reports of this phenomenon in surface reactions.[19–21] While stochastic simulations of those systems have been reported, to the best of our knowledge, analytical studies of external noise affecting the reaction kinetics in CO oxidation are lacking.

The aim of this work is to describe and to apply adiabatic reduction techniques to study theoretically the role of external noise on minimalistic two-variable models for the

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catalytic CO oxidation on Ir(111) and Pt(111). These techniques allow us to obtain a reduced one-variable description from the original set of two-variable Langevin equations. It is shown that external noise induces transitions from mono- to bistability as well as a shift in steady states. Our analytical results are compared with stochastic simulations of the full two-variable systems.

The paper is organized as follows. The minimalistic deterministic bistable catalytic models are presented in Sec. II. This section is also devoted to apply the adiabatic reduction technique to these deterministic systems. In Sec. III, an external noise is imposed on the fraction of CO. A novel extension of the adiabatic reduction technique to this new situation is presented and the phenomena of noise-induced shift of steady states and noise-induced transitions from mono- to bistability are analyzed. Summary and conclusions are presented in Sec. IV.

II. CO OXIDATION ON (111) SURFACES

The CO oxidation on single crystal surfaces can provide an important well-defined example of complex behavior. It is well known that CO oxidation on Pt group metals proceeds via the Langmuir–Hinshelwood mechanism comprising the following steps:[2]

$$CO(gas) + * \leftrightarrow CO(ads),$$

$$O_2(gas) + 2* \rightarrow 2O(ads),$$

$$CO(ads) + O(ads) \rightarrow CO_2(gas) + 2*,$$
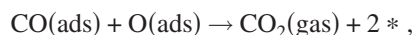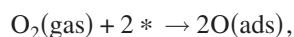
with " *" and "(ads)" denoting a vacant adsorption site and adsorbed molecules or atoms, respectively.

If the surfaces exhibit structural instability with respect to the adsorption of one of the reactants, the CO_2 reaction rate at fixed fluxes directed at the surfaces exhibits oscillatory behavior. The (100) and (110) surfaces of Pt present this particular feature. However, if the surfaces are structurally stable, the reaction rate might only display bistability. In this bistable state, two kinetic stationary states coexist. The active steady state, where the surface is predominantly oxygen covered, and the inactive steady state, where a high CO coverage inhibits O_2 adsorption and hence poison the reaction.[2]

Structurally stable and reactive with respect to CO oxidation are (111) surfaces of Pt or Ir, and kinetic bistability has been experimentally observed in those systems.[22,23] Unlike previous experimental studies, the CO oxidation on Ir(111) was studied in a fashion where the total $CO+O_2$ flux ($\phi_{tot} = \phi_{CO} + \phi_{O_2}$) was held constant and CO ($Y_{CO} = \phi_{CO}/\phi_{tot}$) and O_2 ($Y_{O_2} = 1 - Y_{CO}$) partial contributions varied. Motivated by those experimental studies, this section analyzes minimalist models for CO oxidation on Ir(111) and Pt(111), which take into account a constant total $CO+O_2$ flux, and use as external control parameters the CO fraction Y_{CO} in the total flux and the surface temperature T. We verify that those models exhibit bistability as well as a time scale separation between the variation overtime of the coverages. Later on, we shall use them to study the interplay between kinetic bistability and external noise.

A. Kinetic bistability

We start with CO oxidation on Ir(111). In a simple description one needs to consider only the reaction steps mentioned above. Here, we use the well known mean-field approximation of chemical kinetics, which describes very well the kinetic of CO oxidation on Pt group metals.[24] If the surface concentrations CO(ads) and O(ads) are denoted, in units of monolayers (ML), by θ_{CO} and θ_O, respectively, the state variables are determined by the following two coupled ordinary differential equations:

$$\frac{d\theta_{CO}}{dt} = k_1 Y_{CO}(1 - \theta_{CO}^2) - k_2 \theta_{CO} - k_3 \theta_{CO}\theta_O, \quad (1)$$

$$\frac{d\theta_O}{dt} = k_4(1 - Y_{CO})(1 - \theta_{CO} - \theta_O)^3 - k_3 \theta_{CO}\theta_O, \quad (2)$$

where $k_1 = S_{CO}\phi_{tot}$ and $k_4 = 2S_O\phi_{tot}$, with S_{CO} and S_O representing the initial sticking coefficients for CO and O_2, respectively. ϕ_{tot} is the total $CO+O_2$ flux to the surface mentioned above. This model is very similar to the model introduced by Wehner *et al.*[23] In contrast with previous works,[14,15,23] we consider in our case that while preadsorbed CO inhibits dissociative adsorption of oxygen, no such site-blocking effect is exerted by O(ads) on incoming CO molecules. The exponent 2 in the adsorption rate of CO molecules models the precursor-type kinetics of CO adsorption.[24] The exponent 3 in the adsorption rate of oxygen is a relevant characteristic of the Ir(111) surface.[25,26] It is a consequence of the fact that the growth of the CO_2 rate for small Y_{CO} and above 450 K is not proportional to Y_{CO} as in Pt(111) but to $Y_{CO}^{1.5}$. From a microscopic point of view, the factor 3 may indicate that two hollow sites of the Ir(111) surface, which are two lattice constant apart can only accommodate the two atoms of oxygen if the site in between is also empty. Finally, $k_2 = \nu_d e^{-E_d/RT}$ and $k_3 = \nu_r e^{-E_r/RT}$. For parameters we use the values $\phi_{tot} = 0.878$ ML s^{-1}, $S_{CO} = 1$, $\nu_d = 1 \times 10^{13}$ s^{-1}, $E_d = 140$ kJ/mol, $\nu_r = 10^5$ ML^{-1} s^{-1}, $E_r = 40$ kJ/mol, and $S_O = 0.11$.[14,15,23,26] Note that the rate constants are considered to be independent of coverage. In Fig. 1(a) it is plotted the phase diagram obtained from the stable steady state solutions of Eqs. (1) and (2) as a function of the CO fraction Y_{CO} and temperature T. It shows the bistable regime as observed in experiments.[14,15,23,26]

In order to study bistability in CO oxidation on Pt(111), a similar version of the model introduced by Bär *et al.*[24] is considered. In contrast with the original model, a constant total $CO+O_2$ flux (ϕ_{tot}) to the surface is used.[23] In this case, the state variables are determined by the following rate equations:

$$\frac{d\theta_{CO}}{dt} = k_1 Y_{CO}\left[1 - \left(\frac{\theta_{CO}}{\theta_{CO}^s}\right)^2\right] - k_2 \theta_{CO} - k_3 \theta_{CO}\theta_O, \quad (3)$$

$$\frac{d\theta_O}{dt} = k_4(1 - Y_{CO})\left[1 - \frac{\theta_{CO}}{\theta_{CO}^s} - \frac{\theta_O}{\theta_O^s}\right]^2 - k_3 \theta_{CO}\theta_O. \quad (4)$$

Here, θ_{CO}^s and θ_O^s are the saturation coverages of adsorbed CO and O, respectively. As before, we also consider $k_1 = S_{CO}\phi_{tot}$ and $k_4 = 2S_O\phi_{tot}$; S_{CO} and S_O are the initial sticking
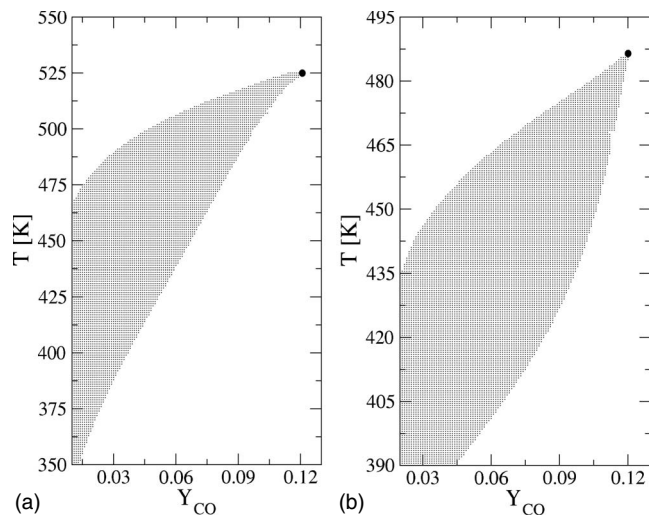
FIG. 1. Phase diagrams for the bistable CO oxidation plotted in the plane spanned by the CO fraction Y_{CO} and the temperature T. The dotted region corresponds to bistable regime as it is obtained by solving the ordinary differential equations. (a) CO oxidation on Ir(111). (b) CO oxidation on Pt(111). Full big circles represent critical or cusp points.

coefficients for CO and O_2, respectively. For simplicity, it is also considered that site-blocking effects are not exerted by O(ads) on incoming CO molecules. The exponent 2 in the adsorption rate of CO molecules models also the precursor-type kinetics of CO adsorption. The exponent 2 in the adsorption rate of oxygen is a relevant characteristic of the Pt(111) surface. It describes the dissociative oxygen absorption reasonably well. Finally, $k_2 = \nu_d e^{-E_d/RT}$ and $k_3 = \nu_r e^{-E_r/RT}$. For parameters we use the values $\phi_{tot} = 0.878$ ML s^{-1}, $S_{CO} = 0.84$, $\nu_d = 1.24 \times 10^{15}$ s^{-1}, $E_d = 146.12$ kJ/mol, $\nu_r = 1.645 \times 10^{14}$ ML^{-1} s^{-1}, $E_r = 100.9$ kJ/mol, $S_O = 0.06$, $\theta_{CO}^s = 0.5$, and $\theta_O^s = 0.25$.[24] Note that the total CO+O_2 flux ϕ_{tot} has the same value than the flux used for Ir(111). Figure 1(b) shows the bistable region obtained from Eqs. (3) and (4). In this case the temperature T_c of the critical point (cusp point) is lower than for the Ir(111) case.

B. Time scale separation and adiabatic reduction

It is clear that the models introduced above can describe very well the bistable behavior observed in CO oxidation on (111) surfaces. In this section we apply the so-called adiabatic reduction technique to those models.[27–30] The aim is to obtain a reduced description that can then be used as the starting point to the stochastic treatment of Sec. III.

Let us start with the catalytic CO oxidation on Ir(111). The starting point is to identify in the model represented by Eqs. (1) and (2) the fast and the slow variables. This can be done by direct numerical integration of those equations, which reveals that a slowly varying trajectory in phase space with low and almost constant oxygen coverage is rapidly reached from any initial condition, which nearly coincides with the nullcline $d\theta_O/dt = 0$.[24] Hence θ_O is the fast variable. This approach is also justified by comparison of the linear relaxation times for the various rate processes $[k_2/[(1-Y_{CO})k_4] \approx 0.1$ for the parameters of Fig. 2(a)]. Figure 2(a) shows the intersection of the nullclines $d\theta_O/dt = 0$ and
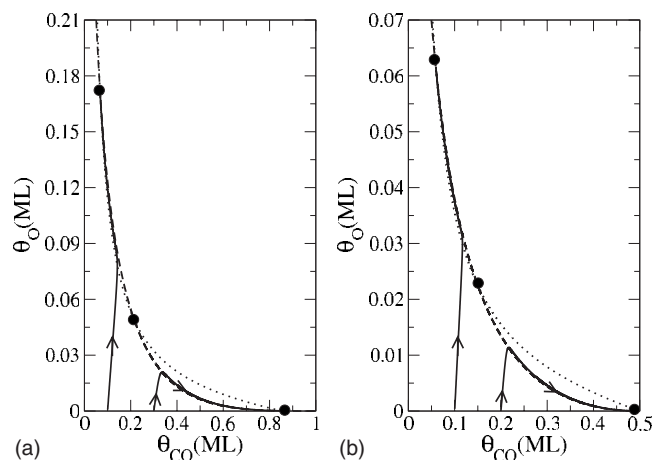

FIG. 2. Phase-space plane of the set of nullclines $d\theta_O/dt = 0$ (dashed line) and $d\theta_{CO}/dt = 0$ (dotted line) obtained from the two-variable models inside the bistable regions in Fig. 1. The two extreme intersections represent stable states and the intermediate intersection corresponds to an unstable solution of the system (full circles). Figures show also several trajectories for different initial conditions (black lines). The oxygen nullcline with low and almost constant oxygen coverage is rapidly reached from any initial condition. (a) CO oxidation on Ir(111) at $Y_{CO} = 0.09$ and $T = 500$ K. (b) CO oxidation on Pt(111) at $Y_{CO} = 0.055$ and $T = 400$ K.

$d\theta_{CO}/dt = 0$ together with two solutions of the system for different initial conditions. This intersection represents bistability for the set of control parameters considered. Note that the nullcline $d\theta_O/dt = 0$ is rapidly reached from any initial condition. Thus, from the analysis mentioned above, the fast variable θ_O is asymptotically at its steady state $\bar{\theta}_O$ obtained neglecting its time derivative. The resulting $\bar{\theta}_O(\theta_{CO})$ is then replaced in Eq. (1) to obtain the following one-variable differential equation:

$$\frac{d\theta_{CO}}{dt} = Y_{CO}k_1(1 - \theta_{CO}^2) - k_2\theta_{CO} - k_3\theta_{CO}\bar{\theta}_O, \tag{5}$$

where

$$\bar{\theta}_O = 1 - \theta_{CO} + \frac{\sqrt[3]{2}\rho\theta_{CO}}{H(\rho, \theta_{CO})} - \frac{H(\rho, \theta_{CO})}{3\sqrt[3]{2}}, \tag{6}$$

with

$$\rho = k_3/k_4(1 - Y_{CO}), \tag{7}$$

and

$$H(\rho, \theta_{CO}) = \{27\rho\theta_{CO}(1 - \theta_{CO}) + \sqrt{108\rho^3\theta_{CO}^3 + [27\rho\theta_{CO}(1 - \theta_{CO})]^2}\}^{1/3}. \tag{8}$$

On the other hand, for the catalytic CO oxidation on Pt(111) the oxygen coverage has already been established as the fast variable by Bär et al.[24] In the work of Bär et al.,[24] a little different model, with the same experimental parameters of the present case, was used. In our particular case, the first step is to identify the fast variable in the model represented by Eqs. (3) and (4). Figure 2(b) shows the corresponding intersection of the nullclines $d\theta_O/dt = 0$ and $d\theta_{CO}/dt = 0$ representing a bistable state. It shows as the nullcline $d\theta_O/dt = 0$ with low and almost constant oxygen coverage is rapidly reached from two different initial conditions. Thus, the oxy-

gen coverage is also the fast variable in this system. Finally, the steady state $\bar{\theta}_O$ is obtained from $d\theta_O/dt = 0$ [Eq. (4)] and the resulting $\bar{\theta}_O(\theta_{CO})$ is then replaced in Eq. (3) to obtain the desired one-variable differential equation.

III. EXTERNAL NOISE ON CO OXIDATION ON (111) SURFACES

Motivated by recent experimental studies,[14,15,23,26] we consider in this section the deterministic models introduced before with the addition of an external noise to the CO fraction Y_{CO} of the total $CO+O_2$ flux. Specifically, Gaussian white noise $\eta(t)$ of zero mean and time-correlations $\langle \eta(t)\eta(t')\rangle = \delta(t-t')$ is introduced by letting $Y_{CO} \to Y_{CO} + r\eta(t)$, r being the noise intensity. This means that the models for CO oxidation on Ir(111) and Pt(111) will include a multiplicative noisy term. Such stochastic processes can be studied using Langevin equations or the corresponding Fokker–Planck approach.[31,32] These two approaches will be used in Sec. III A in the context of an extension of the adiabatic reduction technique. Note that similar reduction techniques have been already implemented to describe stochastic surface reactions where fluctuations are due to finite-size effects (internal fluctuations).[9,12] Here, we extend these ideas to surface reactions under external noise.

A. Adiabatic reduction from the stochastic approach

First, it is considered that the time scale separation holding in the deterministic systems is still valid for appropriate small noise intensity r, such that we can still somehow identify θ_{CO} as the slow variable and θ_O as the fast variable. Then, we devise a method to eliminate the fast variable by taking into account the stochastic effects.

Let us present our method by using a general system of stochastic differential equations (Stratonovich interpretation) for θ_{CO} and θ_O, where an external Gaussian white noise $\eta(t)$, with the properties mentioned above, is imposed in one of the control parameters,[31]

$$\frac{d\theta_{CO}}{dt} = f^{CO}(\theta_{CO},\theta_O) + rg^{CO}(\theta_{CO},\theta_O)\eta(t), \qquad (9)$$

$$\frac{d\theta_O}{dt} = f^{O}(\theta_{CO},\theta_O) + rg^{O}(\theta_{CO},\theta_O)\eta(t). \qquad (10)$$

As in the deterministic adiabatic reduction, we first eliminate the fast variable and replace it in the equation for the slow variable.

We assume that the dynamics of the fast variable θ_O leads to a conditional probability distribution $P(\theta_O|\theta_{CO};t)$ that tends rapidly toward a monomodal sharply peaked function, which is well approximated by a Gaussian distribution.[9,33] In this approximation, the maximum of the steady state probability, which coincides with the average value $\bar{\theta}_O = \langle \theta_O \rangle$, can be calculated by using Novikov's theorem for the noise term of Eq. (10),[1,34]

$$f^{O}(\theta_{CO},\bar{\theta}_O) + \frac{r^2}{2}g^{O}(\theta_{CO},\bar{\theta}_O)\frac{\partial g^{O}(\theta_{CO},\bar{\theta}_O)}{\partial \bar{\theta}_O} = 0. \qquad (11)$$

Solving for $\bar{\theta}_O$ as a function of θ_{CO}, it can then be substituted into Eq. (9). The problem is then reduced to a one-variable Langevin equation,

$$\frac{d\theta_{CO}}{dt} = f^{CO}(\theta_{CO},\bar{\theta}_O) + rg^{CO}(\theta_{CO},\bar{\theta}_O)\eta(t), \qquad (12)$$

with the associated Fokker–Planck equation

$$\frac{\partial P(\theta_{CO};t)}{\partial t} = \frac{\partial}{\partial \theta_{CO}}\left[-f^{CO}P + \frac{r^2}{2}g^{CO}\frac{\partial(g^{CO}P)}{\partial \theta_{CO}}\right], \qquad (13)$$

where $P(\theta_{CO};t)$ is the one-variable probability distribution with steady state maxima obtained from solving[34]

$$F \equiv f^{CO}(\theta_{CO},\bar{\theta}_O) - \frac{r^2}{2}g^{CO}(\theta_{CO},\bar{\theta}_O)\frac{\partial g^{CO}(\theta_{CO},\bar{\theta}_O)}{\partial \theta_{CO}} = 0. \qquad (14)$$

Finally, a phase diagram, which takes into account the effects of external noise in the parameter space (Y_{CO}, T), can be now obtained by solving simultaneously Eqs. (11) and (14). Bistability regions appear now as the set of parameters for which multiple stable solutions of those equations exist.

In summary, a simple approximation has been obtained after adiabatic elimination of the fast oxygen coverage in the stochastic approach. In Sec. III B we will use this approach to analyze the phenomena induced by external noise on CO oxidation on (111) surfaces.

B. Application to CO oxidation on Ir(111)

It is immediate, following previous notation, to identify $f^{CO}(\theta_{CO},\theta_O)$, $f^{O}(\theta_{CO},\theta_O)$, $g^{CO}(\theta_{CO},\theta_O)$, and $g^{O}(\theta_{CO},\theta_O)$ from Eqs. (1), (2), (9), and (10). We follow the approach developed above to study the maxima of the probability distribution of the CO coverage. We focus our attention on two phenomena that have received recent experimental attention:[16] the shifts of the maxima and the appearance of new maxima in the probability distribution.

1. Noise-induced shift of steady states

The existence of shifts in the maxima of the probability distributions induced by external-noise is well known and it has been studied theoretically and experimentally in different contexts.[1,34] It was only recently that this phenomenon was experimentally reported in catalytic surface reactions. Particularly, in the catalytic CO oxidation on Ir(111), it was observed that maxima of the probability function for the reaction rate shift away from the deterministic values of the starting location.[16] We now analyze theoretically the existence of this noise-induced shift by using the reduced algebraic Eqs. (11) and (14) obtained after adiabatic reduction in oxygen coverage.

Solutions of $F=0$, see Eq. (14), represent stable and unstable steady states of the system. For illustration, the parameters Y_{CO} and T are fixed in a region of the parameter space
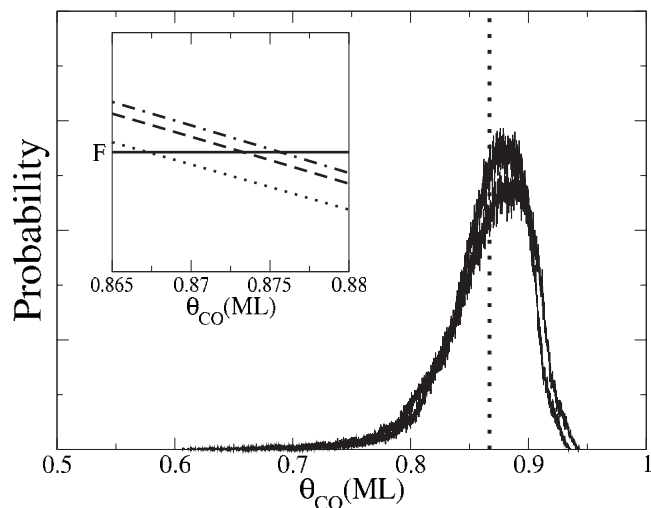
FIG. 3. Noise-induced shift of steady states in CO oxidation on Ir(111) at $Y_{CO}=0.1$ and $T=500$ K, and various noise intensities r. Probability distribution function of θ_{CO} from simulations of the two-variable stochastic system for two values $r=0.08$ and 0.095 for noise intensity. The dotted line represents the approximated position of the deterministic steady state ($r=0.0$). Inset shows F vs θ_{CO} for $r=0.0$ (dotted line), 0.08 (dashed line), and 0.095 (dotted dashed line).

where the deterministic system ($r=0$) is in a monostable steady state of high CO concentration. The inset of Fig. 3 shows that an increase in the noise intensity r leads to an increase in the most probable CO coverage. In the main plot of Fig. 3 we compare this analytical prediction with direct simulations of the Langevin Eqs. (9) and (10). The probability distribution function from numerical simulations is plotted for two different values of noise intensity r. Here, it is clear that the maximum shifts away from the deterministic value. In addition, there is the occurrence of an increasing asymmetry of the probability as already reported in experimental studies of Hayase *et al.*[16]

2. Evidence for noise-induced transition from mono- to bistability

One of the interesting consequences of external noise imposed on nonlinear dynamical system is that the number of maxima of a stationary probability can change as a function of the noise intensity.[1,34–36] In this section, we show theoretical evidence that external noise, in the form imposed in this work and in previous experimental studies,[23] is able to induce transitions from mono- to bistability.[23] This means that the number of maxima in the probability distribution can change from one to two as a function of the noise intensity r and for appropriate values of the CO fraction Y_{CO} and temperature T.

Figure 4(a) plots F for two values of noise intensity r at parameter values $T=520$ K and $Y_{CO}=0.097$. When $r=0$, the system is deterministic, and the existence of a single solution of $F=0$ predicts that trajectories will relax to a monostable state (dotted line), a result confirmed in Fig. 4(b) where we plot trajectories coming from a numerical integration of the full two-variable deterministic systems [Eqs. (1) and (2)]. If
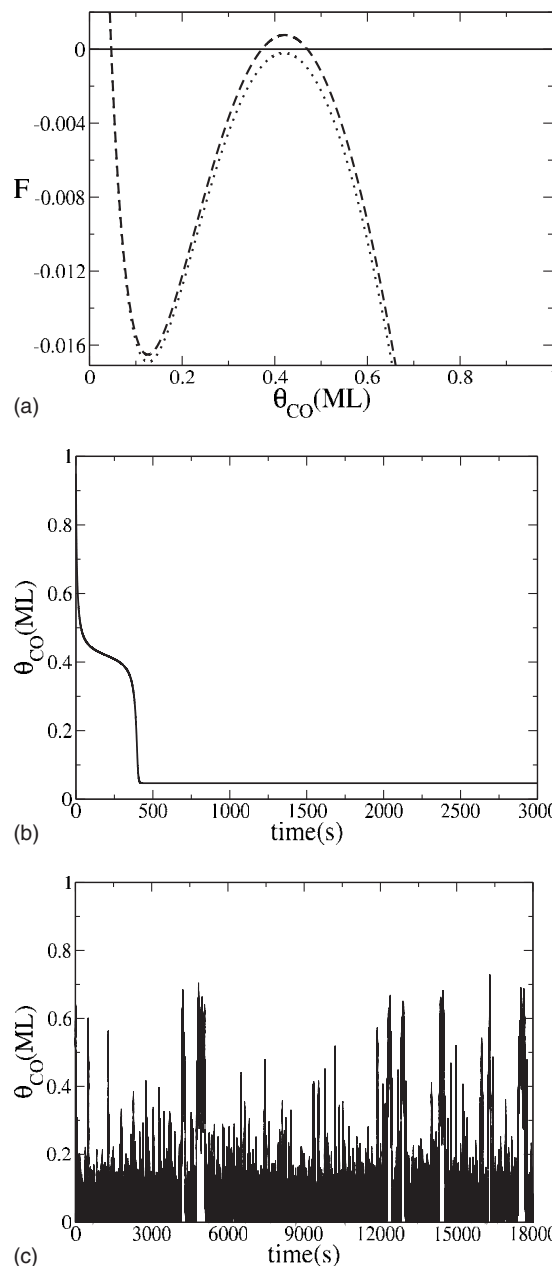

FIG. 4. Noise-induced transitions from mono- to bistability in CO oxidation on Ir(111) at $T=520$ K and $Y_{CO}=0.097$. (a) F vs θ_{CO} for $r=0.0$ (dotted line) and 0.06 (dashed line). (b) Time series of θ_{CO} from simulations of the two-variable deterministic system with initial condition $(\theta_{CO}^0, \theta_O^0) = (0.95 \text{ ML}, 0.0 \text{ ML})$. (c) Time series of θ_{CO} from stochastic simulations of the two-variable stochastic system for $r=0.06$ with initial condition $(\theta_{CO}^0, \theta_O^0) = (0.55 \text{ ML}, 0.0 \text{ ML})$.

the noise intensity increases, a transition to a bistable behavior, characterized by two stable steady states separated by an unstable one, is induced (dashed line). The corresponding trajectories, see Fig. 4(c) for $r=0.06$, do not relax to a single value but behave randomly leading to a steady-state probability distribution with two maxima. Thus, it is clear that external noise induces bistability as well as transitions between the stable steady states. Note that the residence time on the new state of high θ_{CO} is shorter as predicted by the theoretical solution plotted in Fig. 4(a), which shows that the new stable state is closer to separatrix centered on the intermediate unstable state.
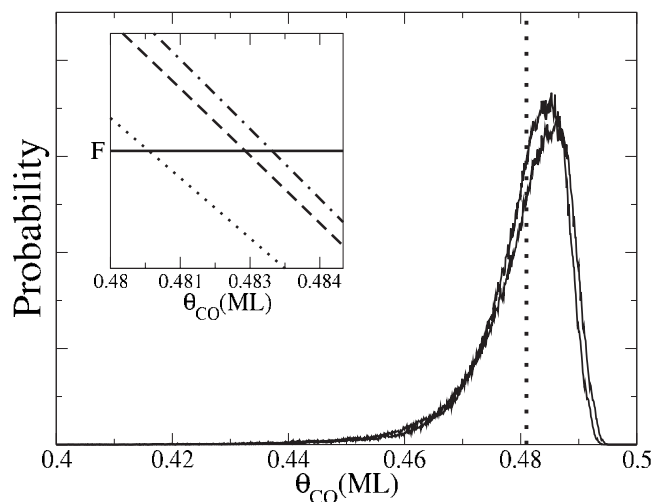
FIG. 5. Noise-induced shift of steady states in CO oxidation on Pt(111) at $Y_{CO}=0.12$ and $T=450$ K. Probability distribution function of θ_{CO} from simulations of the Langevin equations for two values $r=0.1$ and 0.115 for noise intensity, from left to right. The dotted line represents the approximated position of the deterministic steady state. Inset shows F vs θ_{CO} for $r=0.0$ (dotted line), 0.01 (dashed line), and 0.115 (dotted dashed line).

C. Application to CO oxidation on Pt(111)

The same analysis is performed to the catalytic CO oxidation on Pt(111). Again, the external noise is imposed on the CO fraction Y_{CO} of Eqs. (3) and (4) and the maxima of the stationary probability function for θ_{CO} are the important variables to study. They are also given by the solution of the algebraic Eqs. (11) and (14) with $f^{CO}(\theta_{CO}, \theta_O)$, $f^O(\theta_{CO}, \theta_O)$, $g^{CO}(\theta_{CO}, \theta_O)$, and $g^O(\theta_{CO}, \theta_O)$ obtained from Eqs. (3), (4), (9), and (10). In the following, the phenomena of noise-induced shift of steady states and transitions to bistability are analyzed.

1. Noise-induced shift of steady states

We show that external noise can induce a shift in steady states or maxima of probability functions in CO oxidation on Pt(111). For $r=0$, $Y_{CO}=0.12$, and $T=450$ K, the deterministic model predicts a monostable steady state. When the noise intensity r increases, the maxima, as given by the solutions of $F=0$, shift away of the deterministic value, see inset of Fig. 5. In Fig. 5, the probability function is also obtained from direct integration of the corresponding set of stochastic equations. It is clear that the maximum shifts away from the deterministic value when the noise intensity increases. In addition, an increasing asymmetry of the probability function is observed.

2. Evidence for noise-induced transition from mono- to bistability

We show now evidence for external noise induced transitions to bistability in CO oxidation on Pt(111). Figure 6(a) plots F for two values of noise intensity r. The external control parameters are $T=470$ K and $Y_{CO}=0.075$. For $r=0$, the system relaxes to a monostable state (dotted line). When the noise intensity increases to $r=0.07$, a transition to a bistable regime occurs (dashed line). In order to verify those predictions, Fig. 6(b) shows the time series of θ_{CO} obtained from
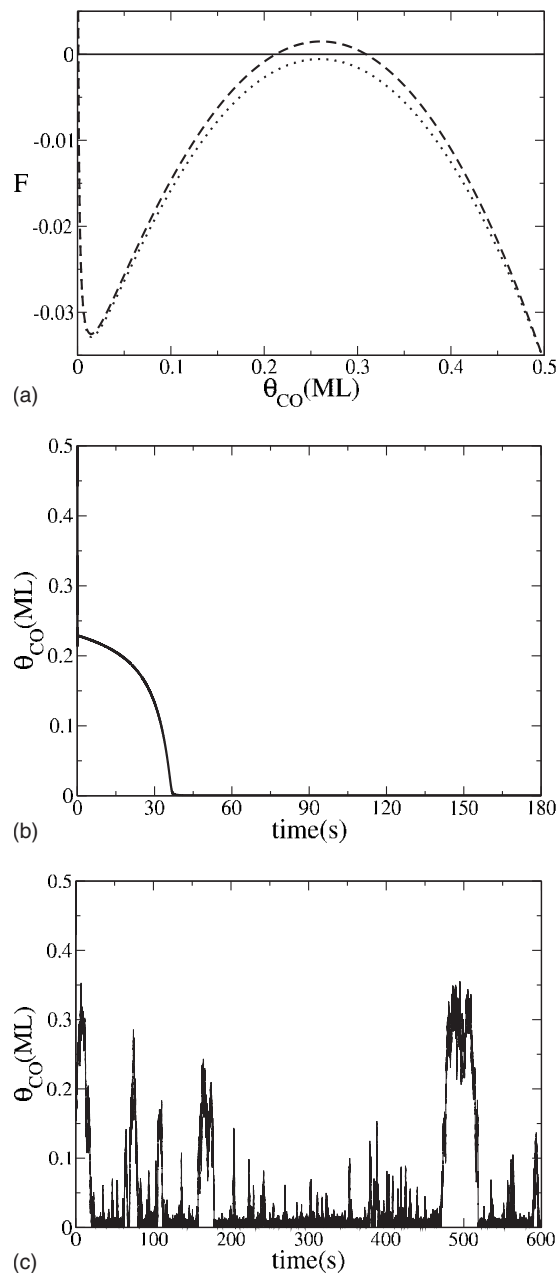

FIG. 6. Noise-induced transitions from mono- to bistability in CO oxidation on Pt(111) at $T=470$ K and $Y_{CO}=0.075$. (a) F vs θ_{CO} for $r=0.0$ (dotted line) and 0.07 (dashed line). (b) Time series of θ_{CO} from simulations of the two-variable deterministic system with initial condition $(\theta_{CO}^0, \theta_O^0)$ $=(0.49$ ML, 0.0 ML). (c) Time series of θ_{CO} from stochastic simulations of the two-variable stochastic system for $r=0.07$ and initial condition $(\theta_{CO}^0, \theta_O^0)=(0.5$ ML, 0.0 ML).

simulations of the two-variable deterministic system, Eqs. (3) and (4). In this case, the trajectory relaxes to a monostable state of very low θ_{CO}. Nevertheless, if the noise intensity increases to $r=0.07$ [see Fig. 6(c)], a transition to a bistable behavior with random transitions between steady states is obtained. As for the cases of Ir(111), the residence time on the new state of high θ_{CO} is shorter as predicted by results of adiabatic reduction [see Fig. 6(a)].

IV. SUMMARY AND CONCLUSIONS

In this work, the influence of external noise on two simplistic models for the catalytic CO oxidation on the structur-

ally stable and reactive Ir(111) and Pt(111) surfaces was studied. First, deterministic surface reaction models were analyzed. Similar to recent experimental studies,[14–16,23,26] the CO oxidation on Ir(111) was studied in a fashion where the total $CO+O_2$ flux ϕ_{tot} is held constant and vary CO (Y_{CO}) and O_2 ($1-Y_{CO}$) partial contributions. The CO oxidation on Pt(111) was also studied in this way. Those deterministic models reproduce bistability. Here, it was shown that in or near the region where bistability is observed, the oxygen coverage is always low and approximately constant (because the reaction is rather rapid) and the CO coverage is often large. Thus, a time scale separation between the variation over time of the oxygen coverage and the CO coverage exists. It allows a reduction in the models by the adiabatic elimination of the fast oxygen coverage (quasisteady state approximation). Second, an external noise is superimposed on the fraction of CO in the constant gas flow directed at the surfaces. A novel scheme is introduced in order to perform adiabatic elimination of oxygen coverage from the set of stochastic equations. The phenomena of noise-induced shift of steady states, which was observed in recent experimental studies of CO oxidation on Ir(111)[15,16,23,26] and noise-induced transition from mono- to bistability have been theoretically and numerically reported. The analytical results have been found to be in reasonable agreement with stochastic simulations of the full two-variable stochastic systems.

It is important to emphasize that throughout the paper real diffusion of adsorbed particles was not considered. Although, the mean-field models used in this work describe very well the interplay between bistability and noise, future studies should include correct particle diffusion in order to analyze the interplay between pattern formation and external noise.[16,17,37–39] In this case one has to distinguish between spatially homogeneous noise and spatiotemporal noise. Analytical studies of external noise imposed on the surface temperature should also be considered in future works.[23] The results reported in this work could stimulate new theoretical and experimental studies in order to understand the role of noise in nonlinear catalytic reactions on other single crystal surfaces.[40] Particularly, experiments of CO oxidation on Pt(111) under external noise are desired in order to verify the theoretical predictions for this system. We also hope that new experiments, under appropriated control parameter conditions, could report the phenomenon of noise-induced transitions from mono- to bistability in CO oxidation on (111) surfaces predicted by our work.

ACKNOWLEDGMENTS

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