Fluctuation-Induced Transitions in a Bistable Surface Reaction: Catalytic CO Oxidation on a Pt Field Emitter Tip

Yu. Suchorski,[1] J. Beben,[2] E. W. James,[3] J. W. Evans,[3] and R. Imbihl[1]
[1]*Institut für Physikalische Chemie und Elektrochemie, Universität Hannover, Callinstrasse 3-3a, D-30167 Hannover, Germany*
[2]*Institute of Experimental Physics, University of Wroclaw, Plac Maxa Borna 9, PL-50-204 Wroclaw, Poland*
[3]*Ames Laboratory and Department of Mathematics, Iowa State University, Ames, Iowa 50011*

(Received 10 September 1998)

Fluctuations which arise in catalytic CO oxidation on a Pt field emitter tip have been studied with field electron microscopy as the imaging method. Fluctuation-driven transitions between the active and the inactive branch of the reaction are found to occur sufficiently close to the bifurcation point, terminating the bistable range. The experimental results are modeled with Monte Carlo simulations of a lattice-gas reaction model incorporating rapid CO diffusion. [S0031-9007(99)08595-6]

PACS numbers: 82.65.Jv, 61.16.Ch, 82.20.Mj

Fluctuations are always present in chemical reaction systems due to the stochastic nature of the elementary processes including reaction and diffusion. In small scale systems, these fluctuations can become prominent and, as a consequence, one may observe new types of behavior not predicted by macroscopic (mean-field) rate laws [1–3]. In bistable systems, for example, such rate laws predict that the system resides on one of two steady-state branches for an indefinite period of time, whereas noise can cause a finite system to fluctuate between these two "stable" states. Mainly because of discrepancies from the predictions of macroscopic rate laws, noisy systems have attracted considerable theoretical interest [1–3]. There have also been experimental studies, e.g., of photosensitive reactions subject to *external* noise [2], and of intermittency in single-molecule spectroscopy studies [4], but few studies of the effect of fluctuations due to *internal* noise in nonlinear reaction-diffusion systems.

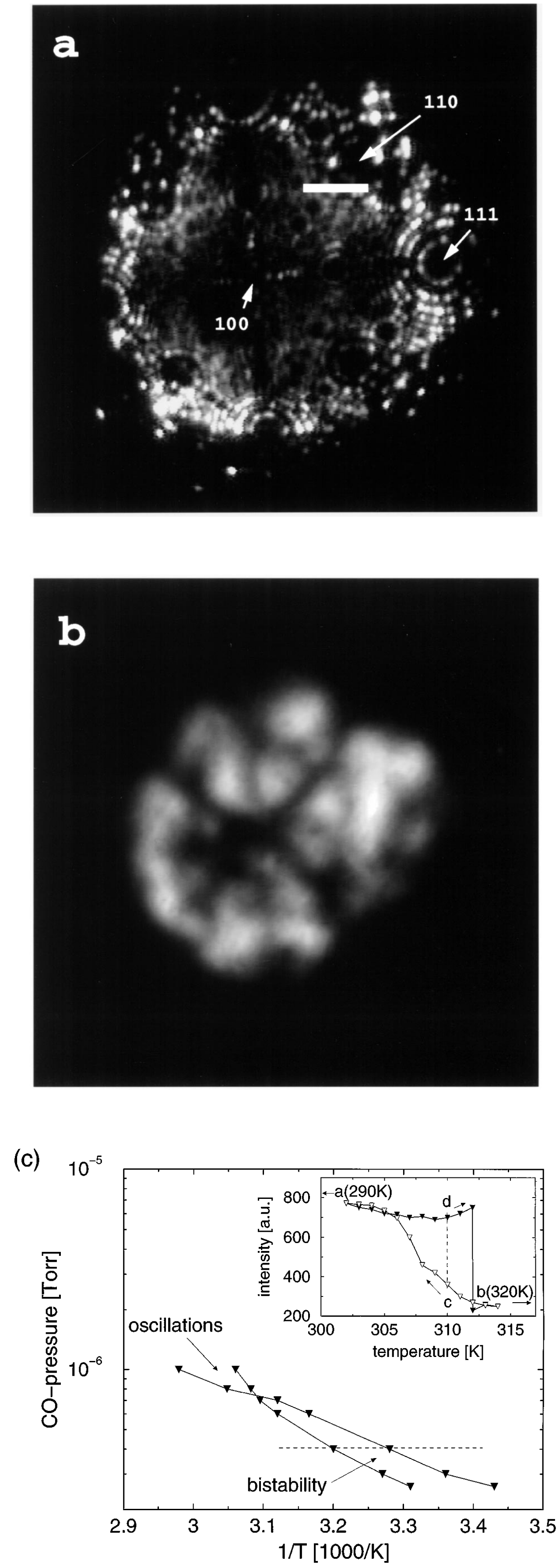
In heterogeneous catalysis, sufficiently small systems to be strongly influenced by fluctuations (i.e., a few hundred up to a few thousand reacting particles) are provided by the facets of a field emitter tip [5], by nanostructured composite surfaces [6], and by the small metal particles (10–100 Å) of a supported catalyst [7]. Since supported catalysts represent the workhorse of real catalysis, an understanding of the reaction behavior of small systems bears also very practical ramifications. In this Letter, we report on the observation of fluctuation-induced transitions in the bistable CO + O_2 reaction on a Pt field emitter tip. We compare these observations with results from Monte Carlo simulations of a surface reaction model which realistically describes key features of CO oxidation including rapid CO diffusion (cf. Ref. [8]).

We employ field ion microscopy (FIM) with its high resolution of 3–4 Å [Fig. 1(a)] to identify the surface crystallography of the area probed by field electron microscopy (FEM) under reaction conditions with a much lower resolution of 20 Å [9]. The FEM video images (40 ms/frame) were digitized with 8 bit resolution. In the following, we focus on a 20×200 Å^2 area in the vicinity of the (110) facet, indicated by the window in Fig. 1(a). We note that the imaging field of 0.4 V/Å associated with FEM does not lead to detectable effects on the reaction [10].

The bifurcation diagram for catalytic CO oxidation for the [001]-oriented tip used in our experiments is displayed in Fig. 1(c). The reaction exhibits two branches which coexist in the bistable range: an active branch in which the surface is predominantly oxygen covered so that CO can still adsorb and react and an inactive branch on which a high CO coverage inhibits O_2 adsorption and hence poisons the reaction [11]. Remarkably, although the various orientations on the tip differ quite strongly in their reactivity (due to different oxygen sticking coefficients) [11], fast CO diffusion apparently ties the different facets together so that the tip behaves as one dynamical system.

In the following, we vary temperature as the fiburcation parameter (for fixed p_{CO} and p_{O_2}) in the bistable region as indicated by the horizontal dashed line ($p_{\mathrm{CO}} = 4 \times 10^{-7}$ Torr) in Fig. 1(c). A hysteresis results as displayed in the inset of Fig. 1(c). Local time series are obtained by integrating the FEM brightness in a small 20×20 Å^2 area inside the window marked in Fig. 1(a). The local brightness in FEM is low when the surface is oxygen covered (high work function), and it is high for a bare or CO-covered surface (low work function). The different time series displayed in Fig. 2(a) correspond to a CO-covered (inactive) and an oxygen-covered (active) surface in the monostable range [a, b in Fig. 1(c) inset] and to states in the bistable range [c, d in Fig. 1(c) inset] of the reaction.

From the time series, probability distributions of the intensity fluctuations have been constructed [Fig. 2(b)]. In the monostable ranges (a and b) relatively narrow distributions of roughly Gaussian shape are found, but in the bistable range the distributions become rather broad. On the active branch, the peak just broadens and becomes slightly asymmetric (c), but on the inactive branch (d) the distribution actually becomes bimodal. This bimodal



distribution is evidence for fluctuation (noise)-induced transitions between the two stable states, where the system is typically in one of these states and spends comparatively little time in transition between them. We emphasize that for smaller p_{CO} (i.e., further from the bifurcation point terminating the bistable range), the distributions remain roughly Gaussian even in the bistable range; i.e., no transitions were observed.

For the same p_{O_2}, p_{CO} parameters, fluctuations have also been studied on several other facets of the Pt tip [12]. In the bistable range, one typically finds strongly broadened probability distributions with shape and asymmetry depending on the specific orientation, but a clear bimodal distribution was seen only in the vicinity of Pt(110). Spatial correlations in the fluctuations in this range typically extend over 100–200 Å on a single facet (reaching into the vicinal planes) [12], but they do not extend between different facets. Thus, although strong coupling via CO diffusion leads to identical bifurcation behavior, the fluctuations on different facets still retain local characteristics.

Next we turn to the theoretical modeling. Previous work considered transitions induced by *external* noise in bistable systems described by simple potential models [2], fluctuations in homogeneous chemical reactions [3], and even a noise-induced transition to bistability in a deterministically monostable surface reaction model [13]. However, to model the observed behavior, we need a realistic model for CO oxidation incorporating *internal* noise resulting from the stochastic nature of adsorption, desorption, reaction, and diffusion. The model must account for the fact that rapid CO diffusion plays an important role in quenching fluctuations [8,14], but that adspecies interactions which induce spatial ordering [15], as well as bifurcation behavior, can compensate this. Atomistic lattice-gas (LG) models have such potential, but most simulations of CO oxidation are based upon ZGB (Ziff-Gulari-Barshad) models [16], which exhibit unrealistic oxygen poisoning and neglect essential processes like CO diffusion.

Thus, here we present results from Monte Carlo simulations of a refined LG model for CO oxidation on surfaces which incorporate the following key features:

(i) CO(gas) adsorption onto single empty sites at rate p_{CO}. CO(ads) hops very rapidly to other empty sites on the surface, so it is assumed that it is randomly distributed on sites not occupied by O(ads) (neglecting

FIG. 1. Catalytic CO oxidation on a Pt field emitter tip. (a) FIM image showing the crystallography of the Pt tip ($T = 78$ K, imaging gas Ne, field strength $F = 3.6$ V Å^{-1}). The rectangular window indicates the area in which fluctuations were studied. (b) FEM image of the same area (same scale) shown in (a) under reaction conditions ($T = 310$ K, $p_{\mathrm{O}_2} = 4.0 \times 10^{-4}$ Torr, $p_{\mathrm{CO}} = 4 \times 10^{-7}$ Torr, $F = 0.4$ V Å^{-1}). (c) Bifurcation diagram for catalytic CO oxidation on a [100]-oriented Pt tip at $p_{\mathrm{O}_2} = 4.0 \times 10^{-4}$ Torr. The inset shows the hysteresis in local FEM brightness (20×20 Å^2) for the area marked in (a) upon cyclic variation of T: filled triangles, heating; empty triangles, cooling.

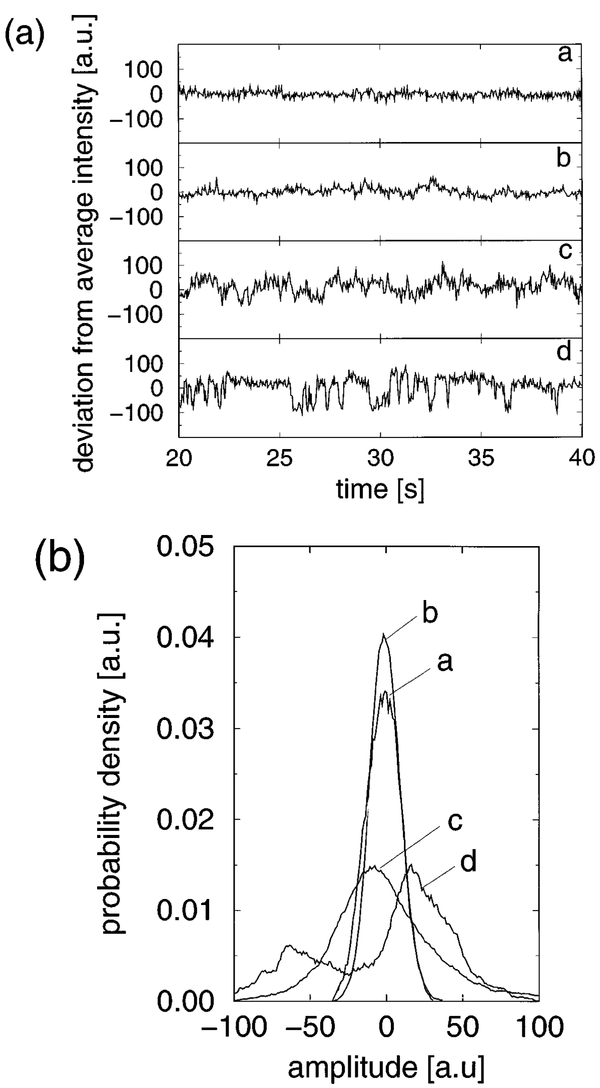


FIG. 2. Fluctuations in catalytic CO oxidation on Pt under different reaction conditions. (a) Time series of the local (20 × 20 Å^2) FEM brightness in the area marked in Fig. 1(a). The data were recorded at different points marked on the hysteresis loop in the inset of Fig. 1(c). (b) Probability distributions corresponding to the time series shown in (a).

CO-CO and CO-O interactions). CO(ads) also desorbs from the surface at rate d.

(ii) O_2(gas) adsorption dissociatively at diagonal nearest-neighbor (NN) empty sites at rate p_{O_2}, *provided* that the *additional* six sites adjacent to these are not occupied by O(ads). This "eight-site rule" [17] reflects the very strong NN O(ads)-O(ads) repulsions. O(ads) is also immobile and cannot desorb, so O(ads) never occupies adjacent sites.

(iii) Each adjacent pair of CO(ads) and O(ads) can react at rate k to form CO_2(gas).

Since CO(ads) is randomized, we adopt a "hybrid" approach [8]: CO(ads) is described by a single mean-field-like parameter, the coverage of CO(ads), but the distribution of O(ads) is described by a full lattice-gas simulation on a square grid of adsorption sites. Our model is still simplistic, but including infinite NN O-O repulsions introduces expected superlattice O-ordering and eliminates artificial ZGB-type O-poisoning [16]. Also, O(ads) interior to $c(2 \times 2)$ O-domains is reactive as found in some experiments [18]; the total reaction rate is in fact given *exactly* by $4k\theta_{CO}\theta_O/(1 - \theta_O)$. Desorption is included in the model since, although T is low in these experiments compared to single-crystal studies, the surface coverages are high reducing the activation barrier for desorption [19].

We first present simulation results for large systems, setting $p_{CO} + p_{O_2} = k = 1$. The model supports bistability (i.e., a stable reactive state with low θ_{CO} coexists with a relatively inactive state with higher θ_{CO}) for sufficiently low d. The width of the bistable region decreases with increasing d, vanishing at a critical value of $d_c \approx 0.054$, which corresponds to a cusp bifurcation [see Fig. 3(a)]. Similar to a thermodynamic critical point, the amplitudes of the rms fluctuations in θ_{CO} and θ_O increase as d increases towards d_c [cf. Fig. 3(b)]. Also, the fluctuations in θ_{CO} are anticorrelated with those in θ_O. We further find "critical slowing down" approaching the critical point, i.e., an increase in decay times of the time-autocorrelation functions obtained from the coverage fluctuations.

Only for small systems (as in the experiments) are these fluctuations sufficient to induce transitions between the stable steady states. Here we show that our model for a "small" 60 × 60 site lattice (with periodic boundary conditions) both mimics and elucidates this behavior. Varying p_{CO} for fixed $d = 0.05$ "close" to d_c, the θ_{CO} distribution is monomodal in both the monostable regions (see curves a–d in Fig. 4), but it has a bimodal or distorted monomodal form in the middle of the bistable region (for an observation time of 3200 time units). The former is expected. The latter indicates the occurrence of transitions between the bistable states which are not frequent on the time scale of observation (resulting in

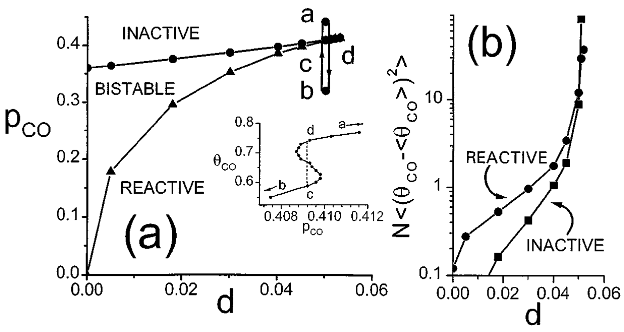


FIG. 3. (a) Bifurcation or phase diagram for our reaction model showing the bistability region. The inset shows hysteresis in θ_{CO} for fixed $d = 0.05$. In the experiment [Fig. 1(c)] the temperature corresponds to d. (b) Amplitude of fluctuations in θ_{CO} for the reactive and inactive branches at the midpoint of the bistability region. N denotes the system size in number of sites.

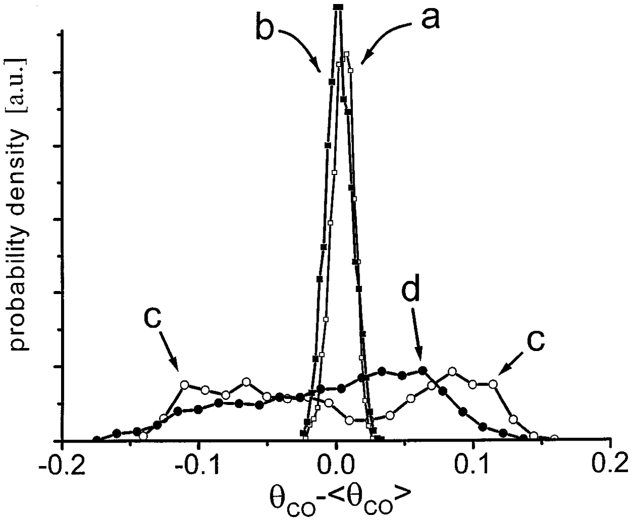


FIG. 4. Probability distributions for θ_{CO} on a 60 × 60 lattice with $d = 0.050$ for points marked on the hysteresis loop in Fig. 3(a).

differences between curves b and c). However, for $d = 0.04$ well below d_c, the θ_{CO} distribution (not shown) is monomodal even in the middle of the bistable region. All these aspects of fluctuation behavior are seen in the experiments.

Clearly, for our model, fluctuation-induced transitions between the bistable states become more likely closer to the critical point d_c, as the amplitude of the fluctuations increases [see Fig. 3(b)]. In the middle of the bistable region, for our observation time, the transition from monomodal to bimodal distributions occurs for $d \approx 0.045$ for a 60 × 60 site system, but it occurs earlier for smaller systems, e.g., at $d \approx 0.040$ for a 30 × 30 site system. Very close to d_c, it becomes difficult to resolve the bimodal distribution because the fluctuations become large, and the distinction between the two steady states diminishes.

In conclusion, we have demonstrated experimentally and theoretically that fluctuation-induced transitions can occur in a bistable surface reaction (i) if the system is sufficiently small and (ii) if the system is in close proximity to a critical point where bistability vanishes and fluctuations diverge. These results are important for understanding the reaction behavior of small sized (nanoscale) systems which can be found in many different areas in chemistry and biochemistry.

E. W. J. and J. W. E. were supported by the Division of Chemical Sciences, U.S. DOE, through Ames Laboratory (operated by ISU under Contract No. W-7405-Eng-82); Yu. S., J. B., and R. I. were supported by the Deutsche Forschungsgemeinschaft.

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