Spatiotemporal Patterns of External Noise-Induced Transitions in a Bistable Reaction-Diffusion System: Photoelectron Emission Microscopy Experiments and Modeling

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The rate of CO oxidation on Ir(111) surfaces exhibits bistability at $T = 500$ K in a range of the CO fraction Y in the CO + O reactant gas flux. Measured CO_2 rates as a function of the noise strength imposed on Y are well reproduced by parameter-free modeling. We present photoelectron emission microscopy measurements and 2D calculations of the spatiotemporal patterns of CO- and O-rich domains. The role of combined multiplicative and additive noise on Y for CO and O domain wall motion and island nucleation-growth-coalescence processes is analyzed.

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The experimental and theoretical investigation of reaction-diffusion (RD) systems is a growing part of the field of pattern formation [1]. Among the most interesting experimental results in the field of autocatalytic chemical reactions are the observation of Turing patterns [2,3], of self-replicating spots [4] (which also triggered substantial theoretical interest [5,6]), and of solitonlike behavior [7].

A recent review on the influence of noise on pattern formation illustrates that there is a rich body of theoretical work [8]. Experimentally, however, much less work has been done, compare, e.g., Ref. [9].

Last year the influence of multiplicative temperature noise [10] and of the noise superposed on the CO + O flux [11] for the CO-oxidation reaction on Ir(111) has been reported. In these studies experimental measurements of the CO_2 rate were combined with the numerical results obtained from 1D and 2D investigations of the associated reaction-diffusion equations in the deterministically bistable regime of this reaction. Among the phenomena found were bistability, transitions from the upper to the lower branch of the bistable loop and vice versa, island nucleation and growth, as well as noise-induced rate bursts and switching. At that time, however, the spatial patterns could be inferred only from the numerical results of the RD model, since the experiments were restricted to CO_2-rate measurements.

In this predominantly experimental Letter we present PEEM (photoelectron emission microscopy) results, which address the question how noise influences the spatiotemporal dynamics of the CO oxidation on Ir(111). PEEM is the method of choice for the investigation of these processes in real time and space [12], since CO and O covered areas on the Ir(111) surface turn out to exhibit sufficient work function contrast. In addition, we give results of numerical calculations using the RD system mentioned above.

The CO_2 rate of the CO-oxidation reaction on Ir(111) exhibits bistability in a restricted temperature range, $400 < T < 550$ K, and specific CO fractions Y in the total CO + O reactant gas flux. At 500 K bistability is observed between $Y = 0.07$ and 0.13 [13], apparent through CO_2 rates measured while ramping Y up from 0 to 0.3 and down from 0.3 to 0. In the bistability range, at one appropriate Y, two CO_2 rates, high or low, can be measured, either during ramping Y up or down and, accordingly, the CO_2 rates vs Y plot displays a hysteresis with upper and lower rate branches.

Intuitively and correctly, one assumes that improperly regulated T and Y would replace the hysteresis phenomenon: at large enough random noise components ΔT and/or ΔY the bistability should vanish. The CO-oxidation reaction on Ir(111) surfaces is somehow unique, since the rates of CO adsorption and desorption, O adsorption, CO + O reaction, and CO and O diffusion are known rather precisely. The partial differential equations that control the rate of CO_2 can be formulated in a mesoscopic model and have been discussed in detail in Refs. [10,11].

By imposing noise ΔY on Y one gets multiplicative as well as additive noise components in the expression for the CO_2 rate. A study of the consequences of white Gaussian noise ΔY on the CO_2 rate revealed experimentally as well as theoretically that with increasing noise amplitudes the hysteresis gets narrower on the Y scale and eventually vanishes [11]. Experiments and numerical calculations demonstrated that at fixed Y through application of ΔY noise transitions from the upper (lower) to the lower (upper) branch of the hysteresis can be induced. Depending on the noise strengths, the time required to complete the transition spans the range from a few seconds (large ΔY) to several hours (small ΔY). Calculations based on the model also reproduced the experimental observation that at large amplitudes of ΔY the CO_2 rate exhibits at a fixed Y bursts from a low rate to a high rate or even switches between the two branches of the rate hysteresis [11]. Outside the region of deterministic bistability only noise-induced rate bursts and rate switching were observed.

The present experiments were performed in a UHV chamber equipped with a long time (> 10 h) stability

PEEM instrument and a D_2 discharge lamp for UV photon generation [14]. For the images shown in the present work, the diameter of the instrument's field of view was set to 310 μm. The temperature of the Ir(111) crystal was held constant at 500 K to a precision that excluded any temperature noise related effects [8]. The reactant gases were directed at the surface via a doser tube. The intrinsic noise on Y was $\Delta Y = 0.001$, given by the specification of the computer-controlled mass-flow controllers in the CO and oxygen supply lines which regulated the constant total gas flux Φ, Y, and ΔY. The ΔY noise component was shaped as Gaussian white noise; see [10,11] for details. PEEM pictures were recorded at a fixed location on the 9 mm diameter crystal as a function of Y, ΔY, and time t in 3 s intervals with 2.86 s integration times of the CCD camera. Because of the work function contrast at the used photon energy, in the PEEM pictures shown below, oxygen covered fractions of the surface appear black, CO covered fractions appear gray, and uncovered regions appear light gray.

The experiments were performed near the low Y border of the rate hysteresis, as indicated in the icon shown in the upper left of Fig. 1. We note that the location of the hysteresis in the present experiments is shifted with respect to our previous work [11], since the total gas flux in the PEEM chamber was about a factor of 1.15 higher. This icon illustrates schematically the bistable CO_2 rate vs Y dependence in the Y range of interest. The initial state of the system at the selected Y, $Y = 0.11$, was prepared on the lower branch of the rate hysteresis (open circle in the icon), and beginning at $t = 0$ external noise ΔY was applied. Accordingly, for all ΔY the surface was set to full CO coverage at $t = 0$ and the PEEM images displayed a gray appearance.

Figures 1 and 2 display PEEM pictures recorded during experiments with varied ΔY. These pictures span time periods from several hours to a few minutes. As seen in Fig. 1(a), at $\Delta Y = 0.02$, 9300 s after the start of the application of external noise on Y, on the lower left of the PEEM image the border of an oxygen island moves into the field of view. This island grows slowly inward, a second oxygen island occurs, these two islands merge, and finally the surface in the field of view is O covered and remains so for the next 12 000 s. Apparently, the initially CO covered surface (low CO_2 rate branch of the hysteresis) was converted into an O covered surface (high CO_2 rate branch) via nucleation and growth of a few O islands. The speed of the walls between the CO and O domains is very slow at the given external ΔY noise, about 0.02 μm/s.

As seen in Fig. 1(b), at increased noise level, $\Delta Y = 0.03$, the transition from a CO covered surface to an O covered one is significantly faster, completed in only about 5000 s. In contrast to the phenomenology seen in Fig. 1(a), in this transition the growth of several oxygen islands is involved. The islands seen in Fig. 1(b) are not circular, but exhibit an ellipsoidal shape. This feature might stem from structural anisotropies on the surface like steps.

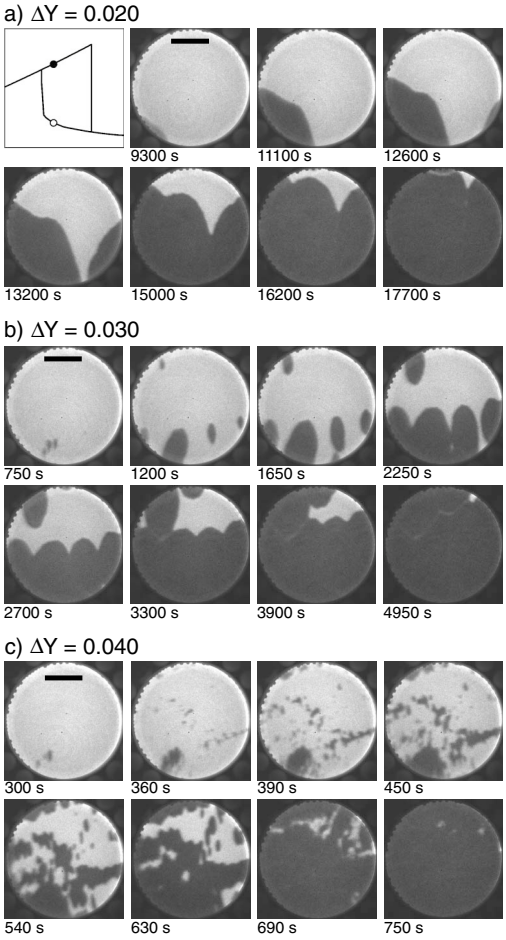

FIG. 1. (a) Upper left: icon that schematically illustrates the hysteresis and the starting point (open circle) of the present measurements; subsequent pictures: PEEM images recorded during the ongoing reaction at $Y = 0.11$ and a noise level of $\Delta Y = 0.02$. Noise application started at $t = 0$ s. Oxygen covered areas are black, and CO covered areas are gray. The horizontal black bar corresponds to 100 μm. (b) PEEM images recorded at $Y = 0.11$ and $\Delta Y = 0.03$. (c) PEEM images recorded at $Y = 0.11$ and $\Delta Y = 0.04$.

For $\Delta Y = 0.04$, Fig. 1(c), the CO-rich to O-rich transition on the surface is completed in only about 800 s. Many O-rich islands with a quite irregular shape are born, grow, and eventually coalesce. At later times than those covered by Fig. 1 the PEEM pictures exhibit a black field of view; i.e., the surface remains O covered and exhibits a high CO_2 rate for the time covered by the experiments.

Application of a $\Delta Y = 0.08$ noise level changes these features. As seen in Fig. 2 which spans a range of about 10 000 s, the CO-rich surface is initially transformed into an O-rich one via small islands birth and growth within 285 s. This state is, however, not permanent, but switches back to a CO-rich state at about 1000 s. During the next 1650 s O islands birth, growth, and coalescence transform the surface back to O-rich conditions. Subsequently, the surface switches back and forth between CO-rich and O-rich states via two phenomenologies: (a) islands of O

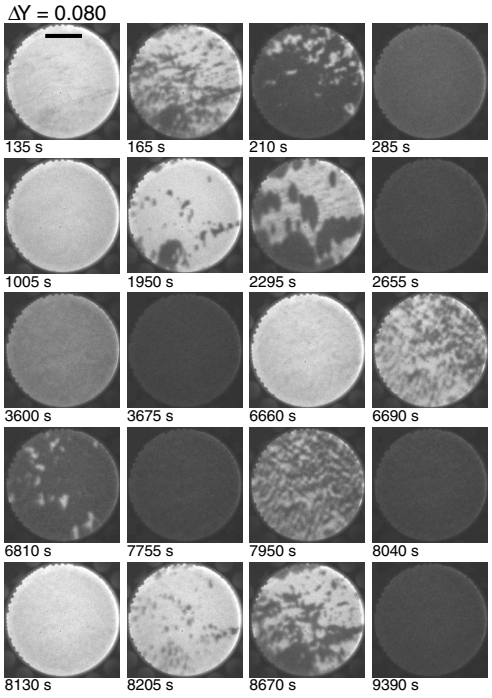

FIG. 2. Sequence of PEEM images recorded at $Y = 0.11$ and $\Delta Y = 0.08$. Other details are as in Fig. 1.

or CO occur, grow, and coalesce in the background of a CO or O-rich surface, (b) the whole surface gets transformed from a CO or O-rich state into a O or CO-rich state within less than 100 s and sometimes within 3 s.

The phenomenologies of the spatiotemporal structures seen in Figs. 1 and 2 are different. In Fig. 1 noise levels from $\Delta Y = 0.02$ to 0.04 cause the surface to convert from the less stable CO covered state into the more stable oxygen covered state in which the surface remains. In Fig. 2 with an applied noise level of $\Delta Y = 0.08$ the surface switches between these states. Since the O-rich state exhibits larger reactivity, the patterns seen in Fig. 1 correspond to a transition from a low CO_2 rate to a high rate, whereas the patterns in Fig. 2 correspond to CO_2 rate bursts and switches. Exactly this phenomenology was observed in our previous study [9].

A graphical representation that condenses the information from hundreds to tens of thousands of PEEM images in a more compact way obtained by software-based data reduction is given in Fig. 3. Shown are the measured gray values along a vertical 270 μm long pixel line (y axis) in the center of PEEM pictures. The picture in Fig. 3(a) corresponds to the sequence shown in Fig. 1(a), and the motion of a single domain wall is easily recognized. The pattern in Fig. 3(b) illustrates that at a significant noise amplitude the initial CO-rich to O-rich transition occurs via multidomain growth and is followed by occasional

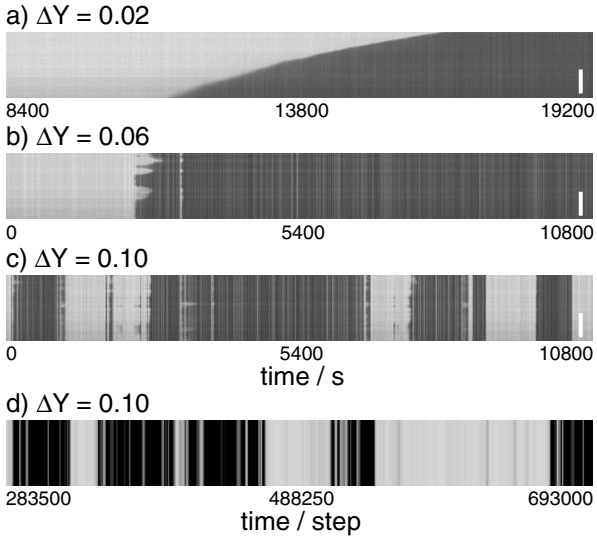

FIG. 3. (a) Time series along a vertical pixel line in the center of PEEM images recorded at $Y = 0.11$ and $\Delta Y = 0.02$. The white bar corresponds to 100 μm. (b) As (a) but at $\Delta Y = 0.06$. (c) As (a) but at $\Delta Y = 0.10$. (d) Calculated time series along a vertical pixel line for $\Delta Y = 0.10$.

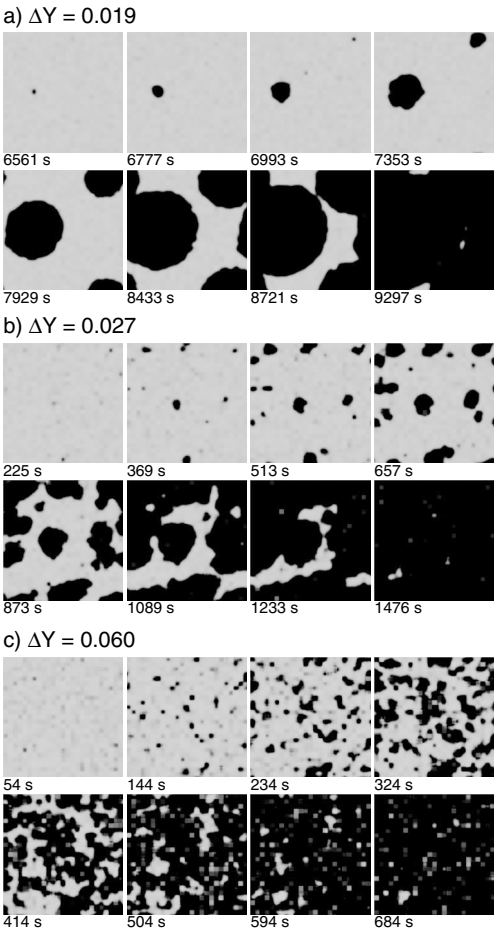

FIG. 4. Domain pattern development with time (oxygen black, CO gray) calculated with the reaction-diffusion differential equations and varied noise level on Y. The initial conditions in the calculations correspond to the open circle in the icon shown in Fig. 1.

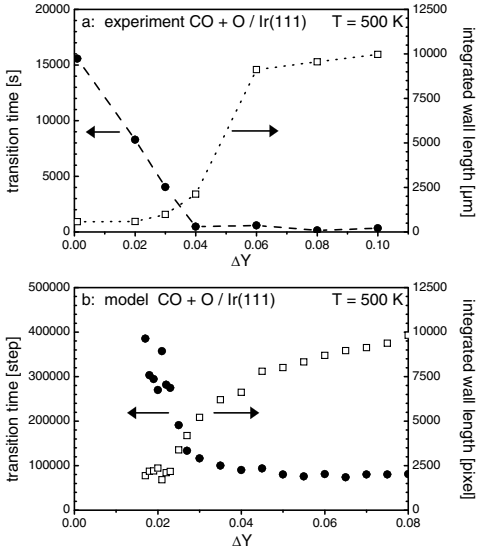

FIG. 5. Circles: Time required to complete the transition from a CO covered to an O covered surface (gray to black in PEEM pictures) as a function of the applied noise level ΔY. Squares: Maximum integrated wall lengths of all domains in PEEM patterns recorded in an experiment as a function of the noise level. (a) Experiment and (b) model.

switches between the O-rich surface and a CO-rich surface. The pattern in Fig. 3(c) was taken along a vertical pixel line in the center. Since for other locations on the surface the same features were observed, it is clear that the noise-induced pattern changes occur homogeneously on the surface.

For the CO-oxidation reaction on Ir(111), the system of kinetic equations including diffusion and noise application is available from our earlier studies [10,11]. These equations were numerically solved on a 500×500 grid using the same approach as presented in [9]. The calculated evolution of the CO/oxygen domain pattern with time for three noise levels is shown in Fig. 4. The same initial conditions as in the experiments were applied. At a small noise level, Fig. 4(a), few oxygen domains develop on the CO covered surface and grow at a very small rate. This phenomenon compares very well with the experimental result shown in Fig. 1(a). At an intermediate noise level, Fig. 4(b), the density of oxygen islands is bigger and their growth rate larger, as seen in Fig. 1(b). At a high noise level, Fig. 4(c), many small islands occur and grow fast, as seen in the experimental data shown in Fig. 1(c). Model calculations performed for an even higher noise level ($\Delta Y = 0.10$) reveal switching and bursts as displayed in Fig. 3(d) in agreement with the experimental data shown in Fig. 3(c).

For quantification of the pattern developments apparent in Figs. 1–3, as well as from the numerical results, characteristic time and length quantities have been extracted. The times needed by the system to change from a fully CO covered state into a fully O covered state (or vice versa) are displayed in Fig. 5 by dots, and the maximum integrated wall lengths of islands that occurred at a selected noise amplitude are shown as squares. It is seen that the qualitative impression one has from the pattern development is nicely represented in Fig. 5: the transitions get faster and the island density larger with increasing noise amplitude. The comparison between the experimental [Fig. 5(a)] and the numerical data [Fig. 5(b)] illustrates that the numerical calculations cover the key features observed in the experiments. The diagram also suggests that the concept of domains and wall motion speeds, which is very well applicable below a noise level of 0.04, somehow loses its meaning above a noise level of 0.05. Above this level the total length of the ''domain'' coastlines approach a value that is the upper limit set by the minimum island area ($30\ \mu m^2$) recognized by the pattern analysis program. Likewise, at these noise levels the speed of the ''domain walls'' gets so fast, that it cannot be connected with a controlling diffusion process.

To summarize, we have shown that in the hysteretic region the dynamics of CO oxidation on Ir(111) surfaces is dominated by domain formation and wall motion for small to moderate noise strength. For larger noise amplitudes we observe fast switching between O and CO dominated surfaces as well as nucleation and growth of the minority phase in the majority phase.

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