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Percolative diffusion of CO during CO oxidation on Pt(100)

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Abstract

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Percolative diffusion of CO during CO oxidation on Pt(100)

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During CO-oxidation on Pt(100), CO diffuses in a “disordered environment” produced by a complex pattern of reconstructed and unreconstructed regions of the substrate. Macroscopic diffusion of CO is effectively only possible on percolating 1×1 -regions of the substrate. We treat the spatio-temporal behavior observed in this reaction system accounting in the simple way for the percolative nature of CO-diffusion. This is done via incorporation into the reaction-diffusion equations of a suitable chemical diffusion coefficient, exploiting ideas from the theory of transport in disordered media. We use these equations to analyze the propagation of reactive, O-rich pulses into a CO-covered 1×1 -background. © 1996 American Institute of Physics. [S0021-9606(96)02709-X]

I. INTRODUCTION

A rich variety of spatial pattern formation and wave propagation phenomena have been observed recently in surface reactions on single crystal surfaces under ultrahigh vacuum conditions. A characteristic length scale of such features is typically of the order of $10\ \mu$. The reactions studied most intensively have involved either CO-oxidation or NO-reduction.¹⁻³ The observed spatio-temporal features reflect the rapid diffusion of such adspecies as CO or NO. (Note that any adsorbed O present is relatively immobile.) More specifically, these features depend on the *chemical* or *collective* diffusion coefficients for the mobile adspecies, which appear in the reaction-diffusion equations describing the evolution of the system. These diffusion coefficients are typically assumed constant, but are in fact highly nontrivial, depending on the locally equilibrated state of the highly mobile adspecies and its local environment. They describe and are defined in terms of the response of the system to *macroscopic spatial inhomogeneities*.⁴

In this contribution, we consider exclusively CO-oxidation on Pt(100).⁵ An important feature of this system is that the clean Pt(100) surface undergoes a “hex”-reconstruction, but significant local coverages of CO (or O) lift this hex-reconstruction to recover a 1×1 -structure.⁶ In analyzing spatio-temporal behavior in this reaction system, one should regard the highly mobile CO as diffusing in a “disordered environment.” This environment is created in part by the other adsorbed CO molecules, as well as by coadsorbed and relatively immobile O, but also (and perhaps more importantly) by the complex pattern of reconstructed and unreconstructed regions of the substrate induced by chemisorption. Effectively, CO diffusing on the hex-regions of surface is irreversibly captured upon reaching 1×1 -regions.⁷ Thus true macroscopic chemical diffusion of CO is only possible via the 1×1 -regions of the surface, and in configurations where these regions form a *percolating network* (see Fig. 1). Therefore, we conclude that the chemical diffusion coefficient, D_{CO} , for CO can only be nonzero

above the percolation threshold for the 1×1 -regions. See Ref. 8 for a general discussion of transport in disordered percolating systems. The main focus of this contribution is to make a first attempt to incorporate in a simple way this key feature into reaction-diffusion equation modeling.

Before proceeding, we briefly comment on two other issues pertaining to chemical diffusion in surface reactions, and specifically to CO-oxidation. As implied above, D_{CO} is influenced not just by the substrate reconstruction, but also by adspecies interactions. In fact, the CO-CO interactions alone induce a strong dependence of D_{CO} on the local coverage of CO,⁹ an effect which we do not address further here. Another issue arises for reaction systems exhibiting oscillatory kinetics in which there is an associated cyclical nucleation and growth of islands, e.g., of 1×1 -CO islands in CO-oxidation on Pt(100). Here one expects to find atomic-scale spatial structure in the form of growing (or shrinking) islands, even in a *macroscopically spatially uniform state*. The boundaries of such islands are expected to be atomically sharp as a consequence of the strong attractive interactions driving the nucleation process. Sometimes the term “uphill diffusion” is used to describe mass transport to such islands during their growth.¹⁰ Indeed, atomically sharp spatial structures have in fact been observed in recent field emission microscopy and field ion microscopy studies of surface reactions,³ including CO-oxidation on Pt tips.¹¹ Furthermore, the mean-field reaction-diffusion equation formalism was recently modified to describe the evolution of sharp “phase boundaries,” directly relating their existence to attractive adspecies interactions.¹² However, in CO-oxidation on Pt(100), the “uphill diffusion” of CO to growing 1×1 -CO islands, which occurs in a macroscopically uniform system, does not correspond to “chemical diffusion,” in the sense defined above. The atomic scale structure associated with these islands is distinct from the macroscopic spatial variations described by D_{CO} .

In Sec. II, we describe very briefly the model used to analyze CO-oxidation on Pt(100), noting various prescrip-

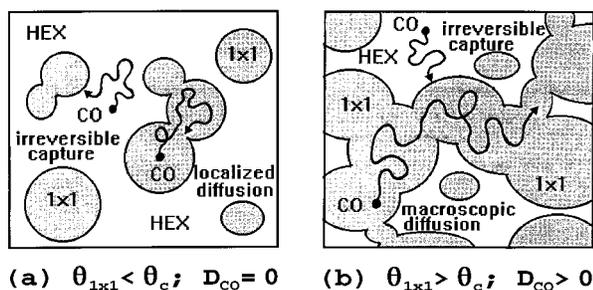


FIG. 1. Schematic showing (a) localized diffusion of CO, with $D_{CO}=0$, on nonpercolating 1×1 -regions when $\theta_{1\times 1} < \theta_c$; (b) macroscopic chemical diffusion of CO, with $D_{CO} > 0$, on percolating 1×1 -regions when $\theta_{1\times 1} > \theta_c$. Here $\theta_{1\times 1}$ is the fraction of the substrate in the 1×1 -state, and θ_c is the percolation threshold.

tions for the reconstruction dynamics, and focusing on our modified treatment of CO-diffusion. We then describe in Sec. III, results for propagation of reactive, O-rich pulses into a CO-covered 1×1 -background. Finally, we summarize our findings in Sec. IV.

II. MODEL FOR CO-OXIDATION ON Pt(100)

The basic model for the CO-oxidation kinetics on Pt(100) was developed by Imbihl *et al.*⁵ One must specify the fraction, $\theta_{1\times 1}$, of the substrate in the 1×1 -state, so then a fraction $\theta_{\text{hex}} = 1 - \theta_{1\times 1}$ is in the hex-state. CO can adsorb on both 1×1 - and hex-regions, so local coverages, $\theta_{CO}^{1\times 1}$ and θ_{CO}^{hex} , are specified for each region. O is assumed to adsorb on and populate only the 1×1 -regions, so that only a single local coverage, $\theta_O^{1\times 1}$, need be specified. Adsorbed O does not inhibit CO-adsorption, which is simply assumed to occur at a constant rate (independent of coverages) in the modeling. However, adsorbed CO does block O-adsorption (on 1×1 -regions), which requires an adjacent “pair of empty sites.”¹³ One key modification to this adsorption scheme is that O can also adsorb at defect sites, even on a CO-covered surface. In this respect, it should be noted that the expansion of the top Pt-substrate layer associated with the hex \rightarrow 1×1 transition forces up Pt atoms which automatically nucleate island “defects” on top of the substrate.¹⁴ Other features of the model include reaction of adjacent CO and O, CO desorption from both regions (both of which produce “empty sites” for O-adsorption), and irreversible transfer of CO from the hex to 1×1 -regions via diffusion-mediated trapping. Explicit expressions for the rates of all these processes, as well as values of associated rate constants, can be found in Ref. 5. These are incorporated into our modeling.

It is also necessary incorporate the dynamics of reconstruction into the modeling. The 1×1 -regions are known to shrink, due to thermally activated reconstruction, when $\theta_{CO}^{1\times 1}$ and $\theta_O^{1\times 1}$ drop below certain critical values, $\theta_{CO}^{\text{crit}}$ and θ_O^{crit} , respectively.⁶ Thus, one has

$$d\theta_{1\times 1}/dt = -k_-(1-c)\theta_{1\times 1}, \quad \text{if } c < 1, \quad (1)$$

where $c = \theta_{CO}^{1\times 1}/\theta_{CO}^{\text{crit}} + \theta_O^{1\times 1}/\theta_O^{\text{crit}}$.⁵ Imbihl *et al.*⁵ assumed that 1×1 -regions expand when $\theta_{CO}^{1\times 1}$ reaches some threshold

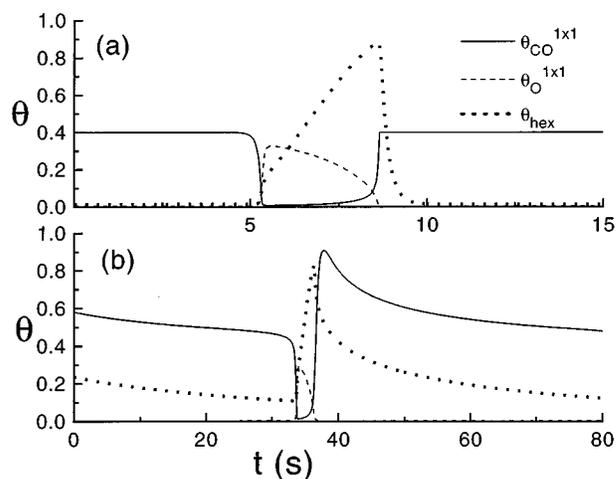


FIG. 2. Oscillatory reaction kinetics for a spatially uniform system using (a) Imbihl *et al.* (Ref. 5) reconstruction dynamics, with partial pressures $P_{CO} = 9 \times 10^{-6}$ Torr and $P_{O_2} = 2 \times 10^{-4}$ Torr; the oscillation period is ≈ 15 s; (b) King and co-workers (Ref. 15) reconstruction dynamics, with $P_{CO} = 8 \times 10^{-6}$ Torr, $P_{O_2} = 1.3 \times 10^{-4}$ Torr; here ≈ 50 s. Most of the oscillation cycle is spent in a CO-covered 1×1 -state.

value, $\theta_{CO}^{\text{grow}}$, in a way so as to maintain $\theta_{CO}^{1\times 1}$ at this value. However, recent experimental studies by King and co-workers¹⁵ of the nonlinear growth kinetics of 1×1 -regions suggest that, more precisely,

$$d\theta_{1\times 1}/dt = k_+(\theta_{CO}^{\text{hex}})^n \theta_{\text{hex}}, \quad \text{if } c \geq 1, \quad (2)$$

where $n \approx 4.1$.

Thus we emphasize that the main difference between the model of King and co-workers,¹⁵ and that of Imbihl *et al.*,⁵ is just in the incorporation by the former of the experimentally determined nonlinear 1×1 -island growth kinetics, rather than a simpler assumed “linear” growth kinetics. A rather different approach by Andrade *et al.*¹⁶ implements a Ginzburg–Landau formalism, based on a suitable Hamiltonian description of the energetics of adsorption and reconstruction. However, such an approach cannot reliably describe the type of *far-from-equilibrium* kinetics associated with substrate reconstruction in this system,¹⁷ as is clear by comparison with Ref. 15. In this work, we incorporate the prescriptions of Refs. 5 and 15 for the reconstruction dynamics, and compare resulting behavior.

Such models reproduce the oscillatory reaction kinetics observed in experiment, for a restricted range of partial pressures of CO and O, and of substrate temperature, T .^{2,5} The steps in the oscillation cycle can be characterized as follows: (i) O adsorbs at defect sites on a CO-covered 1×1 -surface; (ii) this reduces the CO coverage (due to reaction between adsorbed O and CO), and initiates the $1\times 1 \rightarrow$ hex reconstruction; (iii) subsequently most of the adsorbed CO is removed and the O-coverage begins to grow, as do the hex-regions; (iv) eventually the presence of large hex-regions, on which only CO adsorbs, leads to an increase of the CO coverage, corresponding nucleation and growth of 1×1 regions, and finally a return to state (i). Figure 2 shows an example, rel-

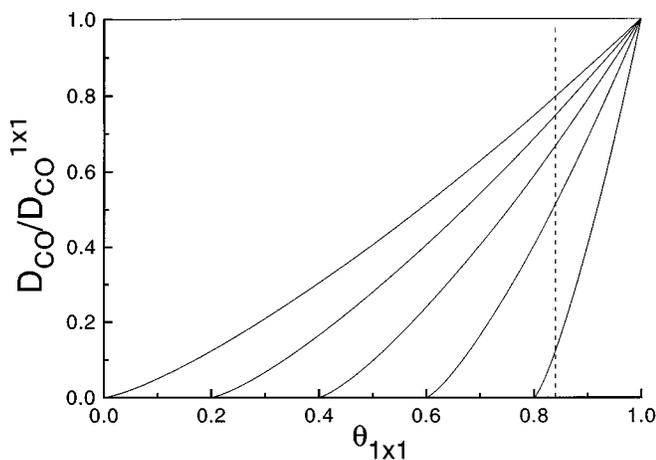


FIG. 3. $D_{\text{CO}}/D_{\text{CO}}^{1\times 1}$ vs $\theta_{1\times 1}$, for various θ_c . The strong decrease in $D_{\text{CO}}/D_{\text{CO}}^{1\times 1}$ with increasing θ_c , for fixed $\theta_{1\times 1}=0.85$ (indicated by a vertical dashed line) is also apparent.

evant to the study in Sec. III, of the oscillatory dynamics using both prescriptions for the reconstruction dynamics. Here the partial pressures and temperature, $T=480$ K, have been chosen such that the system has a long oscillation period, most of which is spent in a predominantly CO-covered 1×1 -state. While in this state, adsorbing O slowly reacts away adsorbed CO until the critical coverage is reached, initiating the “rapid” $1\times 1\rightarrow$ hex transformation and recovery to the CO-covered 1×1 -state. Note that this rapid dynamics similar to that when system is “excited” for higher CO partial pressures just outside the oscillatory regime.

Next we address in more detail the central issue of the description of CO-diffusion in this model. As indicated above, the standard treatments^{2,5,16} just include CO-diffusion on 1×1 -regions. This is consistent with the feature that CO diffusing on hex-regions is effectively irreversibly trapped by 1×1 -regions, and thus cannot undergo macroscopic transport on the hex-regions (when 1×1 -regions are present). However these treatments also set D_{CO} constant, which is not consistent with the fact that chemical diffusion is only possible if the 1×1 -regions percolate. In our analysis, we exploit results from the general theory of transport in percolating systems^{6,18} to make the simplest consistent choice for D_{CO} of¹⁹

$$D_{\text{CO}}(\theta_{1\times 1}) = \left[\frac{\theta_{1\times 1} - \theta_c}{1 - \theta_c} \right]^\mu D_{\text{CO}}^{1\times 1}, \text{ for } \theta_{1\times 1} > \theta_c,$$

and

$$D_{\text{CO}}(\theta_{1\times 1}) = 0, \text{ for } \theta_{1\times 1} < \theta_c. \quad (3)$$

(see Fig. 3). Here θ_c is the percolation threshold for the 1×1 -regions, $\mu \approx 1.3$ is the critical exponent for diffusive transport, and $D_{\text{CO}}^{1\times 1}$ is the diffusion coefficient for CO on a perfect 1×1 -substrate (where $\theta_{1\times 1}=1$). For a simple model involving irreversible nucleation of islands at random locations, and subsequent growth and coalescence, one expects that $\theta_c \approx 0.7$ ML in the regime of “large” characteristic island

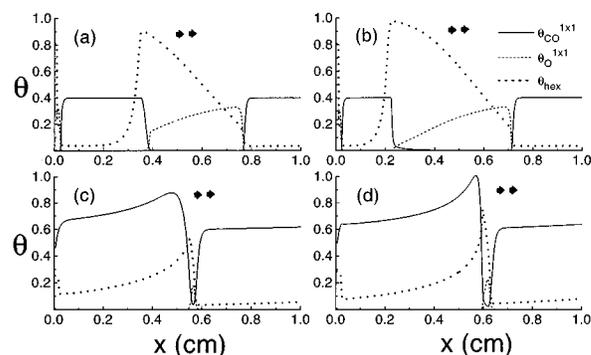


FIG. 4. Snapshots of coverage profiles for reactive pulses propagating to the right; (a)(b) use Imbihl *et al.* (Ref. 5) reconstruction dynamics, and (c)(d) use King and co-workers (Ref. 15) reconstruction dynamics; (a) and (c) incorporate constant D_{CO} ; (b) and (d) incorporate percolative diffusion, with $\theta_c=0.6$.

size.²⁰ However, for diffusion-mediated nucleation and growth, there is a depletion in the population of nearby islands, and θ_c can be as high as 0.8 ML.²⁰ Actually, neither of these analyses apply to the more complicated scenario of reversible growth and shrinkage of islands occurring in the reaction system, so there the value of θ_c is rather uncertain. In fact, the above specification (3) is certainly an oversimplification since D_{CO} really depends on the complete state of the system, which is not determined simply by specifying $\theta_{1\times 1}$. However, (3) is a reasonable first approximation.

III. ANALYSIS OF PROPAGATING REACTIVE PULSES

We now perform an analysis of the experimentally observed^{5,21} excitation of reactive, O-rich pulses into a quiescent CO-covered 1×1 -background. Typically, these pulses are generated by “defect regions” at steps. Again we adopt essentially the same model, and values of all rate parameters, as in Ref. 5, but consider both the prescriptions of Imbihl *et al.*,⁵ and King and co-workers,¹⁵ for the growth of 1×1 -regions. We compare behavior produced by the standard choice of constant D_{CO} with that produced by the form (3), for various θ_c . We choose the surface temperature, $T=480$ K, and partial pressures of CO and O, just as in Fig. 2, so that the homogeneous system has a long oscillation period most of which is spent in the CO-covered 1×1 -state. For our studies of pulse propagation, we take a semi-infinite system with a region of high defect concentration at the left end of width 0.01 cm, characterized by an enhanced defect-mediated adsorption rate for O. After initiating adsorption at $t=0$, the system quickly attains a CO-covered 1×1 -state, into which the defect region excites reactive pulses. Similar behavior is observed if the homogeneous system is not in, but is sufficiently near the oscillatory region that the system is “excitable”.^{22,23} In fact, excitable systems provide a useful generic paradigm for the behavior observed here. Figure 4 shows typical results for coverage profiles obtained by numerical integration of the reaction-diffusion equations with $D_{\text{CO}}^{1\times 1}=4\times 10^{-4}$ cm²/s. (This value of D_{CO} was selected to match the original studies, but is probably substantially

TABLE I. Propagation velocity, V , vs percolation threshold, θ_c , for D_{CO} given by (3) with $D_{CO}^{1\times 1}=4\times 10^{-4}$ cm²/s (except for the top row where $D_{CO}=4\times 10^{-4}$ cm²/s is constant).

θ_c	V (cm/s) (Imbihl)	V (cm/s) (King)
...	0.126	0.0341
0.0	0.123	0.0244
0.2	0.121	0.0263
0.4	0.120	0.0263
0.6	0.116	0.0188
0.8	0.106	0.0140

higher than the actual value.⁵ This affects the calculated values of the propagation velocity, as discussed below.)

First, we provide some general remarks about the observed pulse propagation. At the front of the pulse, CO diffuses to the left, reducing $\theta_{CO}^{1\times 1}$ in the immediate area. This “kicks” the local region into a single oscillation cycle, analogous to the reactive removal of CO in the spatially uniform system. In general, for “strong” oscillations or excitability, and “weak” diffusion, the pulse shape is determined by time-trace of concentrations in the homogeneous system.²³ Different interior points in the pulse simply have different phases in the oscillation cycle, and the width of the pulse is proportional to its velocity. In fact, pulse shapes in Fig. 4 are reproduced very well by mirror image of time-traces in Fig. 2. Next we discuss the expected dependence of the propagation velocity, V , on the choice of D_{CO} . For models with constant D_{CO} , it follows trivially that V is directly proportional to $\sqrt{D_{CO}}$.²² Thus, one expects a decrease in V if one changes from constant D_{CO} to percolative diffusion (3), and as one increases θ_c , since then D_{CO} decreases at any fixed $\theta_{1\times 1}$ (see Fig. 3). Below, we discuss in detail these issues separately for the two different prescriptions for reconstruction dynamics.

For the prescription of Imbihl *et al.*,⁵ a common feature of the reactive pulse, both when D_{CO} is constant [Fig. 4(a)], or given by (3) with $\theta_c=0.6$ [Fig. 4(b)], is an extended interior region with insignificant coverage (and thus diffusion) of CO. Clearly, here, the above mentioned correspondence between pulse shape and time-trace would be precise. However, we find that the length of the pulse is actually shorter in Fig. 4(a), where $V=0.126$ cm/s, than in Fig. 4(b) with smaller $V=0.116$ cm/s. This just reflects the presence of significant CO-diffusion to the right at the tail end of the pulse in Fig. 4(a). This causes the pulse width to shrink relative to Fig. 4(b), where diffusion is inhibited at the tail end of the pulse (since $\theta_{1\times 1}$, and thus D_{CO} , is low there). It is also clear that here V is determined primarily by behavior at the front of the pulse. Thus V will be controlled by the value of D_{CO} in that region, which is determined by the corresponding value of $\theta_{1\times 1}$ [for the case (3)]. Since $\theta_{1\times 1}$ is only slightly reduced from unity at the front of the pulse, D_{CO} is not greatly reduced, even for large θ_c . Indeed, Table I shows that the decrease in V , accounting for percolative diffusion using (3), is not that dramatic.

Finally, we discuss behavior using the prescription of King and co-workers¹⁵ for the reconstruction dynamics. Fig-

ures 4(c) and 4(d) show that the shape of the pulse is very different from the Imbihl model. But perhaps a more important observation is that in the “wake” of each pulse, the hex \rightarrow 1 \times 1 transformation is slow, so $\theta_{1\times 1}$ only increases very slowly back towards unity (and $\theta_{CO}^{1\times 1}$ slowly decreases). Thus, the subsequent excited wave propagates into a medium with changing $\theta_{1\times 1}$ (and $\theta_{CO}^{1\times 1}$), so its velocity and shape is a function of time. Also, since $\theta_{1\times 1}$ is typically significantly below unity when the pulse is emitted, effects of percolative diffusion are expected to be greater. This is clear from Table I which shows that V decreases significantly upon changing from constant D_{CO} to percolative diffusion (3) and increasing θ_c . For consistency here, we always measured V at the point when the value of $\theta_{1\times 1}$ just in front of the pulse was about 0.85. [This is a point in time prior to that shown in Figs. 4(c) and 4(d).]

IV. SUMMARY

We have presented the first treatment of spatio-temporal behavior in CO-oxidation on Pt(100) accounting in a simple way for the percolative nature of CO-diffusion. This is done by selection of a suitable form for the dependence of the chemical diffusion coefficient, D_{CO} , on the fraction, $\theta_{1\times 1}$, of the substrate in the 1 \times 1-state on which true macroscopic diffusion is possible. As expected, we find that this results in a decrease in the propagation velocity of reactive, O-rich pulses excited at defects at steps (compared to the traditional choice of D_{CO} as a constant, with a value equal to that for a perfect 1 \times 1-substrate). For the conditions considered here, the reduction in velocity is not great using the prescription of Imbihl *et al.*⁵ for the reconstruction. This is simply because $\theta_{1\times 1}$ is close to unity at the front of the pulse where the velocity is selected. The effect is naturally greater for the prescription of King and co-workers,¹⁵ where $\theta_{1\times 1}$ is lower at the pulse front. However, we emphasize that for different conditions (e.g., lower CO partial pressure, or increased temperature), one expects that the hex reconstruction will not be so completely lifted during the oscillation cycle of the reaction kinetics. Then the effects of percolative diffusion will be correspondingly greater (for any realistic model).

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¹G. Ertl, Adv. Catal. **37**, 213 (1990).

²R. Imbihl, Prog. Surf. Sci. **44**, 185 (1993).

³R. Imbihl and G. Ertl, Chem. Rev. **95**, 697 (1995).

⁴H. Spohn, *Large Scale Dynamics of Interacting Particles* (Springer, Berlin, 1991).

⁵R. Imbihl, M. P. Cox, G. Ertl, H. Muller, and W. Brenig, J. Chem. Phys. **83**, 1578 (1985); M. P. Cox, G. Ertl, and R. Imbihl, Phys. Rev. Lett. **54**, 1725 (1985).

⁶R. J. Behm, P. A. Thiel, P. Norton, and G. Ertl, J. Chem. Phys. **78**, 7437 (1983).

- ⁷The diffusion or “escape” of CO from 1×1 -regions back to hex-regions is an activated process, in contrast to diffusion in the reverse direction. Thus escape is expected to be significant at higher surface temperatures, but not for temperatures around 480 K of interest here.
- ⁸D. Stauffer and A. Aharony, *Introduction to Percolation Theory* (Taylor and Francis, London, 1992).
- ⁹W. Swiech, C. S. Rastomjee, R. Imbihl, J. W. Evans, B. Rausenberger, W. Engel, A. K. Schmid, A. M. Bradshaw, and E. Zeitler, *Surf. Sci.* **307-309**, 138 (1994).
- ¹⁰D. G. Vlachos, L. D. Schmidt, and R. Aris, *J. Chem. Phys.* **93**, 8306 (1990).
- ¹¹V. Gorodetski, J. H. Block, W. Drachsel, and M. Ehsasi, *Appl. Surf. Sci.* **67**, 198 (1993); V. Gorodetski, W. Drachsel, M. Ehsasi, and J. H. Block, *J. Chem. Phys.* **100**, 6915 (1994).
- ¹²A. Mikhailov and G. Ertl, *Chem. Phys. Lett.* **238**, 105 (1995).
- ¹³One expects that the “pair of empty sites required for O-adsorption must actually be part of a larger ensemble of empty sites. Correspondingly, the probability of finding such a “pair” is taken as $(1 - \theta_{CO}^{1 \times 1} / \theta_{CO}^{\max} - \theta_O^{1 \times 1} / \theta_O^{\max})^2$, where $\theta_{CO}^{\max} = 1/2$ and $\theta_O^{\max} = 3/5$ are the maximum coverages for CO and O, respectively.
- ¹⁴W. Hosler, E. Ritter, and R. J. Behm, *Ber. Bunsenges Phys. Chem.* **90**, 205 (1986); E. Ritter, R. J. Behm, G. Potschke, and J. Winterlin, *Surf. Sci.* **181**, 403 (1987).
- ¹⁵A. Hopkinson, J. M. Bradley, X. C. Guo, and D. A. King, *Phys. Rev. Lett.* **71**, 1597 (1993); A. Hopkinson and D. A. King, *Chem. Phys.* **177**, 433 (1993); M. Gruyters, T. Ali, and D. A. King, *Chem. Phys. Lett.* **232**, 1 (1995).
- ¹⁶R. F. S. Andrade, D. Lima, G. Dewel, and P. Borckmans, *J. Chem. Phys.* **100**, 9192 (1994); R. F. S. Andrade, G. Dewel, and P. Borckmans, *ibid.* **91**, 2675 (1989).
- ¹⁷The Ginzburg–Landau evolution equation for $\theta_{1 \times 1}$ from Ref. 16 includes a Laplacian “diffusion” term, where the “diffusion” coefficient, $D_{1 \times 1}$, is determined by the interfacial energy between adjacent patches of 1×1 - and hex-substrate. Here we note that D_{CO} always includes an analogous contribution due to the spatial coupling associated with reaction of species on distinct (adjacent) sites. See, J. W. Evans and T. R. Ray, *Phys. Rev. E* **50**, 4302 (1994). However, this contribution to D_{CO} , as well as $D_{1 \times 1}$, are very small, and do not play a significant role in spatial pattern formation.
- ¹⁸B. I. Halperin, S. Feng, and P. N. Sen, *Phys. Rev. Lett.* **54**, 2391 (1985); S. Feng, B. I. Halperin, and P. N. Sen, *Phys. Rev. B* **35**, 197 (1987).
- ¹⁹This result for D is often presented in the context of diffusion of a single particle in a disordered environment. However, the same D gives the chemical diffusion coefficient of a non-interacting gas of finite concentration. This follows from simple extension of the analysis of R. Kutner, *Phys. Lett. A* **81**, 239 (1981), for diffusion on a perfect lattice.
- ²⁰D. E. Sanders and J. W. Evans, *Phys. Rev. A* **38**, 4187 (1988); M. C. Bartelt and J. W. Evans, *Surf. Sci.* **298**, 421 (1993); *MRS Proc.* **312**, 255 (1993).
- ²¹H. H. Rotermund, S. Jakubith, A. von Oertzen, and G. Ertl, *J. Chem. Phys.* **91**, 4942 (1989).
- ²²A. S. Mikhailov, *Foundations of Synergetics I* (Springer, Berlin, 1990).
- ²³P. Grindrod, *Patterns and Waves* (Clarendon, Oxford 1991), Sec. 3.3.