Pattern Formation during the Oxidation of CO on Pt{100}: A Mesoscopic Model

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Constantly changing irregular patterns of carbon monoxide (CO) and oxygen are seen during CO oxidation on platinum crystals in the [100] orientation. Ours is the first reaction-diffusion model to reproduce this pattern formation on physically feasible length and time scales, faithfully incorporating the available experimental data. Numerical simulations show patterns made up of CO and oxygen fronts moving at similar speeds to those seen in experiments.

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Spatiotemporal pattern formation occurs in a number of catalytic reactions, such as the Belousov-Zhabotinsky reaction where oscillating spirals and targets are seen [1]. Similar structures form during the catalytic oxidation of carbon monoxide on the surface of single platinum crystals, where patterns comprise areas of different surface phase or covered by different adsorbates. During the reaction, oxygen and CO are adsorbed onto the platinum surface. At high enough temperatures and for certain orientations of the surface relative to the bulk crystal, the presence of adsorbates leads to a phase change, i.e., a rearrangement of the surface platinum atoms. When the oxygen and CO react, carbon dioxide gas is released, and the surface reverts to its original configuration. This cycle can lead to kinetic oscillations in the surface phase. If communication between different areas on the crystal is very rapid compared with the rate of oscillation, the whole surface oscillates in phase; otherwise, there can be phase lags across the surface and spatial patterns arise [2]. There are two main spatial coupling mechanisms: diffusion of CO across the surface, important at low pressures, and global coupling through the gas phase, which dominates at high pressures. The surface orientation has a decisive effect on pattern formation: in the [111] orientation, there is no phase change and hence no patterns, on Pt{110} classical spirals and targets are seen (e.g., [3]), while on Pt{100}, the patterns are typically more irregular [4–6], though circular wave fronts are also seen [5].

In this Letter, we model pattern formation in CO oxidation on a single platinum crystal in the [100] orientation. The kinetic mechanism for this reaction is well established and has been modeled extensively [7–9]. Spatial modelling has concentrated on Pt{110} using a simplified representation of the kinetic mechanism, extended to include diffusion terms (and sometimes gas global coupling) [10]. These models produce results that qualitatively resemble experimentally observed patterns, but they cannot be used for detailed quantitative comparison since both the kinetic and diffusion mechanisms are simplified. Monte Carlo methods are also used, but at present, these must assume unrealistically low diffusion coefficients in order to allow pattern formation on computationally accessible length and time scales [11]. We present a mesoscopic spatial model based on the detailed kinetic mechanism [9] together with diffusion terms derived from a careful consideration of adsorbate migration on the surface. Our model allows the faithful simulation of two-dimensional pattern formation on experimental length and time scales.

The clean Pt{100} surface can be prepared in the metastable bulk-terminated 1 × 1 state at 300 K, with the surface atoms in a square configuration. Above 500 K, the surface restructures into the more stable hex state where the top layer of atoms is arranged hexagonally. Adsorption of CO onto the hex phase lifts the surface reconstruction, causing patches of 1 × 1 to form. The adsorption probability of oxygen on the hex phase is negligible. However, both oxygen and CO stick onto the 1 × 1 surface, where they react. They are then released in the form of CO2 gas, and the clean 1 × 1 phase relaxes back into the hex state. Thus the reaction can lead to oscillations in the surface coverages of hex and 1 × 1 phases and adsorbates. The reaction scheme is adapted from [8,9]

\[
\begin{align*}
\text{CO}_\text{gas} + \text{Pt}_{\{100\}}\text{hex} & \xrightarrow{k_1} \text{CO}_{\text{hex}} \\
\text{CO}_\text{gas} + \text{Pt}_{\{100\}} \times 1 & \xrightarrow{k_2} \text{CO}_{\text{1×1}} \\
\text{CO}_{\text{hex}} + \text{Pt}_{\{100\}} \times 1 & \xrightarrow{k_3} \text{CO}_{\text{1×1}} + \text{Pt}_{\{100\}} \\
\text{1/2O}_2\text{gas} + \text{Pt}_{\{100\}} \times 1 & \xrightarrow{k_4} \text{O}_{\text{1×1}} \\
\text{nCO}_{\text{hex}} + m\text{Pt}_{\{100\}} \text{hex} & \xrightarrow{k_5} \text{nCO}_{\text{1×1}} + m\text{Pt}_{\{100\}} \times 1 \\
\text{Pt}_{\{100\}} \times 1 & \xrightarrow{k_6} \text{Pt}_{\{100\}} \\
\text{CO}_{\text{1×1}} + \text{O}_{\text{1×1}} & \xrightarrow{k_7} \text{CO}_2\text{gas} + 2\text{Pt}_{\{100\}} \times 1
\end{align*}
\]

where adsorbates are denoted by subscripts hex and 1 × 1 and gases by gas. Adsorbed oxygen exists as single atoms in contrast to the molecular oxygen gas. The reaction rates

\[
\begin{align*}
k_1 &= \frac{1}{60} \times \text{molecule/s} \\
k_2 &= \frac{1}{100} \times \text{molecule/s} \\
k_3 &= \frac{1}{100} \times \text{molecule/s} \\
k_4 &= \frac{1}{100} \times \text{molecule/s} \\
k_5 &= \frac{1}{100} \times \text{molecule/s} \\
k_6 &= \frac{1}{100} \times \text{molecule/s} \\
k_7 &= \frac{1}{100} \times \text{molecule/s}
\end{align*}
\]
in ML mbar\(^{-1}\) s\(^{-1}\) are \(k_1 = 2.22 \times 10^5\), \(k_2 = 3.7 \times 10^{12}\) exp\([\frac{-105}{(RT)}]\), \(k_3 = 10^4\) exp\([\frac{-49}{(RT)}]\), \(k_6 = 2.08 \times 10^5\), \(k_7 = 2.0 \times 10^8\) exp\([\frac{-57.6}{(RT)}]\), \(k_8 = 4.9 \times 10^4\) and \(k_9 = 2.5 \times 10^{11}\) exp\([\frac{-108}{(RT)}]\), where \(R = 0.0083\) kJ mol\(^{-1}\) K\(^{-1}\) and \(T\) is temperature. The rates \(k_3\) and \(k_4\) depend on the adsorbate and take the respective values \(10^{15}\) exp\([\frac{-154}{(RT)}]\) and 43 in ML mbar\(^{-1}\) s\(^{-1}\) at zero coverage \([9]\).

Experimental images distinguish between clean surface, oxygen-covered, and CO-covered areas (e.g., \([6]\)). Accordingly, we follow pattern formation using adsorbate

\[
\frac{\partial(\theta_{\text{hex}}^\text{CO})}{\partial t} = k_1 p_{\text{CO}} S_{\text{hex}}^\text{CO} \theta_{\text{hex}}^\text{CO} (1 - \theta_{\text{hex}}^\text{CO}) - k_2 \theta_{\text{hex}}^\text{CO} \theta_{\text{hex}} - k_3 B \theta_{\text{hex}}^\text{CO} (1 - \theta_{\text{hex}}^\text{CO}) + k_4 B \theta_{\text{hex}}^\text{CO} \theta_{\text{hex}}^\text{CO} (1 - \theta_{\text{hex}}^\text{CO}) + k_5 B \theta_{\text{hex}}^\text{CO} (1 - \theta_{\text{hex}}^\text{CO})
\]

\[
+ \min(0, -\theta_{\text{hex}}^\text{CO} \frac{\partial \theta_{\text{hex}}^\text{CO}}{\partial t}) + \max(0, -0.8 \theta_{\text{hex}}^\text{CO} \frac{\partial \theta_{\text{hex}}^\text{CO}}{\partial t}) - D_{\text{hex}} \theta_{\text{hex}}^\text{CO} \theta_{\text{hex}}^\text{CO} \nabla^2 \theta_{\text{hex}}^\text{CO} - D_{\text{hex}} \theta_{\text{hex}}^\text{CO} \nabla^2 \theta_{\text{hex}}^\text{CO}
\]

where \(c(\theta) = \theta_{\text{hex}}^\text{CO}/0.25 + \theta_{\text{O}}^\text{CO}/0.4\), \(n = 4.17\), \(\kappa = 1000\), \(p_{\text{CO}}\), and \(p_{\text{O}}\) are the partial pressures of CO and O\(_2\), respectively, \(S_{\text{hex}}^\text{CO} = 0.78\) and \(S_{\text{CO}}^\text{hex} = 0.91\) at \(\theta = 0\) are the sticking probabilities of CO on hex and 1 \(\times\) 1 phases, \(S_{\text{O}}^\text{CO} = 0.31\) at \(\theta = 0\) is the sticking probability of O\(_2\) on 1 \(\times\) 1 phase, and \(B = 1\) measures the boundary length between the two phases \([9]\). (For \(S_{\text{O}}^\text{CO}\), we use the values given in \([9]\) for recently vacated adsorption sites, and neglect a distinction between these and fully relaxed 1 \(\times\) 1 sites.) We do not include gas global coupling in our model, since the effect is insignificant at the low pressures we consider here \([6,12,13]\).

At phase change, about 20% of atoms are displaced \([14]\), so a surface Pt atom in 1 \(\times\) 1 phase occupies an area about 1.25 times that of a hex phase atom. The max and min terms in the equations account for these surface density changes at both phase change and relaxation and for the resulting displacement of adsorbed CO and oxygen.

Diffusion of CO within 1 \(\times\) 1 and hex patches dominates over cross-phase diffusion which can only occur at phase boundaries. The diffusion rate depends not only on the density of CO in the area from which it leaves, but also on the empty site density where it arrives. The diffusion terms take account of both these observations. \(D_{\text{hex}}\) and \(D_{\text{hex}}\) are half the diffusion coefficients for CO on clean hex and 1 \(\times\) 1 phases; we set them both to be \(10^{-6}\) cm\(^2\) s\(^{-1}\) \([4]\).

At the temperatures we consider, oxygen is essentially immobile.

We simulate two-dimensional (2D) pattern formation on a single 600 \(\mu\)m \(\times\) 600 \(\mu\)m Pt\([100]\) crystal, dividing the surface into a grid of 100 \(\times\) 100 cells. Each cell contains many CO adsorption sites and is larger than the initial size of hex and 1 \(\times\) 1 phase patches, but smaller than the characteristic length scale for pattern formation, thus, our model is mesoscopic. We also perform one-dimensional (1D) integrations on a 6 \(\mu\)m \(\times\) 600 \(\mu\)m ribbon divided lengthwise into 100 cells in the spirit of \([15]\) (but now with a faithful description of the dominant spatial coupling). We integrate the reaction-diffusion equations numerically using Adams-Bashforth time stepping and second-order spatial finite differences with periodic boundary conditions.

Figure 1 summarizes the results of 1D simulations for 10\(^{-6}\) mbar \(\leq p_{\text{CO}} \leq 10^{-5}\) mbar, 10\(^{-5}\) mbar \(\leq p_{\text{O}} \leq 10^{-4}\) mbar at fixed \(T = 480\) K. We start with a clean surface, predominantly in hex phase, where \((\theta_{\text{hex}}^\text{CO}, \theta_{\text{hex}}^\text{O}) = (0.001, 0, 0, 0)\), punctuated by defects where \((\theta_{\text{hex}}^\text{CO}, \theta_{\text{hex}}^\text{O}) = (0, 0.5)\), \((1, 0, 0.5)\), \((0.5, 0.9)\), and \((1, 0, 0.9)\) in cells 1, 38, 56, and 89. The defects represent areas in 1 \(\times\) 1 phase and partially
covered by adsorbed oxygen, inspired by experiments [12] where \( p_{\text{O}_2} \) was set first and then \( p_{\text{CO}} \) increased stepwise. Each simulation was run for 1000 s.

The experimental parameter range for oscillations was mapped for varying \((p_{\text{O}_2}, p_{\text{CO}})\) at constant \( T = 480 \) K [12], revealing three distinct regions of phase space (Fig. 1). Observed oscillations are mainly irregular [6,13,16], suggesting that they are not in phase across the whole surface, and so that spatial patterns may be present. Our simulations also divide \((p_{\text{O}_2}, p_{\text{CO}})\) space into three regions (Fig. 1): low (region \( \alpha \)) and high (region \( \beta \)) \( \text{CO} \) coverage and oscillations (region \( \gamma \)). In region \( \alpha \) (\( \beta \)), representative values of \( 1 \times 1 \), total \( \text{CO} \) \((\theta_{\text{tot}}^{\text{CO}} = \theta_{1\times1}^{\text{CO}} \theta_{\text{hex}}^{\text{CO}})\), and total oxygen \((\theta_{\text{tot}}^{\text{O}} = \theta_{1\times1}^{\text{O}} \theta_{\text{hex}}^{\text{O}})\) coverages are \( 0.31 \), \( 0.13 \), and \( 4.9 \times 10^{-5} \) (0.98, 0.41, and \( 1.4 \times 10^{-4} \)). Regions \( \alpha \) and \( \beta \) merge below region \( \gamma \) via intermediate \( \theta_{\text{CO}}^{\text{O}_{\text{tot}}} \) solutions. However, a significant difference remains between the two regions, with high \( \text{CO} \) solutions developing much faster than those at low \( \theta_{\text{CO}}^{\text{O}_{\text{tot}}} \).

Both model (\( \gamma \)) and experimental (\( \text{C} \)) oscillatory regions are \( V \)-shaped and tilted towards higher \( p_{\text{CO}} \). However, region \( \gamma \) lies at lower \( p_{\text{CO}} \) than region \( \text{C} \). The simulations start with \( p_{\text{CO}} \) and \( p_{\text{O}_2} \) at their target values, whereas experimentally [12] \( p_{\text{PCO}} \) was increased stepwise, giving a lower average value, which might explain the offset. Our oscillations have periods \( P \approx 80 \) s, being shorter in the midrange of \( p_{\text{CO}} \) and for higher \( p_{\text{O}_2} \). Experimentally, a decrease in \( p_{\text{CO}} \) and \( T \) increases the oscillation period [13]. In Fig. 1, we find \( 90 \) s \( \leq P \leq 970 \) s, comparing well with experiments (typically at higher partial pressures), where periods lie in the range 1–4 min for work function oscillations with amplitudes 100–300 mV at \( T = 500 \) K and up to 10 mins or more at lower temperatures [13]. However, using different initial conditions and longer runs, we found periods of up to 2700 s. With small amplitudes, faster oscillations with periods of only a few seconds were found experimentally [13].

Further simulations revealed that bulk initial conditions affect the long-term surface state and can alter the positions of regions \( \alpha \), \( \beta \), and \( \gamma \): low initial \( \text{CO} \) coverage shifts the boundaries towards higher \( p_{\text{CO}} \) and vice versa. The boundaries of experimental region \( \text{C} \) were confirmed by repeatedly increasing and decreasing \( p_{\text{CO}} \): the error bars (not shown in Fig. 1) are quite large, echoing our finding.

We find two types of propagating front: \( \text{CO} \) and oxygen-\( \text{CO} \). \( \text{CO} \) fronts appear for the full \((p_{\text{O}_2}, p_{\text{CO}})\) range, at the beginning of simulations with low \( \theta_{1\times1}^{\text{CO}}, \theta_{\text{hex}}^{\text{CO}} \) and medium/high \( \theta_{1\times1}^{\text{CO}} \) defects in initially high \( \theta_{1\times1}^{\text{CO}} \) bulk coverages. To measure their speeds to 10% accuracy we had to use finer \( 10 \times 10 \) grids. In Fig. 2, the surface initially has high \( \theta_{1\times1}^{\text{CO}} \) coverage and high \( \theta_{1\times1}^{\text{O}} \) develops immediately, with \( \theta_{\text{CO}}^{\text{O}_{\text{tot}}} \) insignificant. A wave of \( \text{CO} \) spreads from the defects pushing out the oxygen ahead. Phase relaxation occurs at the leading edge, shown in the sharp transition between high and low \( \theta_{1\times1}^{\text{CO}} \), so hex phase dominates behind the front, with \( \theta_{\text{CO}}^{\text{O}_{\text{tot}}} \) remaining low and \( \theta_{\text{CO}}^{\text{O}_{\text{tot}}} \) negligible. For higher \( p_{\text{CO}} \) and lower \( p_{\text{O}_2} \), \( \theta_{\text{CO}}^{\text{O}_{\text{tot}}} \) ahead of the front is lower and \( \theta_{1\times1}^{\text{CO}} \) and \( \theta_{1\times1}^{\text{O}} \) behind it are higher, so there is less phase relaxation. The speeds of 1D front are 0.13–14 \( \mu \text{m s}^{-1} \) compared with 2–50 \( \mu \text{m s}^{-1} \) in experiments (at higher partial pressures and for \( 420 \) K \( \leq T \leq 540 \) K) [4,6]. \( \text{CO} \) fronts are slower at higher \( p_{\text{O}_2} \) and lower \( p_{\text{CO}} \) where the phase change is most marked, in accord with the argument [6] that the phase transition slows them.

We also find initial travelling reaction waves triggered by defects and consisting of an oxygen front closely fol-

![Figure 1](https://example.com/fig1.png)

**FIG. 1.** The oscillation regime for our model (\( *, \square, \diamond, \bigcirc, \bigcirc \), and solid lines) is compared to that observed in experiment [12] (+ and dashed lines). Key: \( * \square \diamond \bigcirc \) steady evolution to low/medium/high \( \text{CO} \) state; \( \bigcirc \) regular surface oscillations. Regions \( \alpha \), \( \beta \) and \( \gamma \) show low and high \( \text{CO} \) and 1 \( \times \) 1 coverages and oscillations, respectively, in simulations. Experimental regions \( \text{A} \), \( \text{B} \), and \( \text{C} \) correspond to low and high \( \text{CO} \) coverage and oscillations, respectively.

![Figure 2](https://example.com/fig2.png)

**FIG. 2.** \( \text{CO} \) front propagation in 2D at \( t = 500 \) s: (a) \( \theta_{1\times1}^{\text{CO}} \), (b) \( \theta_{1\times1}^{\text{O}} \) and (c) \( \theta_{1\times1}^{\text{O}_{\text{tot}}} \) (white = 1, black = 0) at \((p_{\text{O}_2}, p_{\text{CO}}) = (6 \times 10^{-5}, 1 \times 10^{-6}) \) mbar for bulk initial conditions \((\theta_{1\times1}^{\text{CO}}, \theta_{\text{hex}}^{\text{CO}}) = (0.735, 2.98 \times 10^{-4}, 0.402, 3.54 \times 10^{-2})\) and \( 2 \times 2 \) cell defects with \((\theta_{1\times1}^{\text{CO}}, \theta_{\text{hex}}^{\text{CO}}) = (1.10 \times 10^{-3}, 0.341, 1.98 \times 10^{-2}) \) and \( \theta_{1\times1}^{\text{CO}} = 0.134, 0.234, 0.334, 0.134, 0.234, 0.334 \) with bottom left corners at \((1,1), (75, 111), (51,91), (121,21), (171, 151), \) and \((7,155)\), respectively, on a \( 200 \times 200 \) grid. The initial front speed is 0.24 \( \mu \text{m s}^{-1} \).
The adsorbed CO is removed as the reaction wave passes, from which we adapted our own. This work was done moving fronts of adsorbed carbon monoxide and oxygen captures pattern formation in this system on experimental irregular [6,13,16]. A 1D front is shown in Fig. 3: an initial fits with the observation that oscillations are typically modelling wave component in many of our oscillatory solutions the ensuing oscillations is shorter. The presence of a travelling wave, but with oxygen following CO, have been observed oxygen-CO fronts move faster [6]. Similar consecutive lines) at times (a) 82 s and (b) 90 s, for bulk initial conditions [5,6] (for higher partial pressures and [Fig. 3(a)] is invaded by oxygen pushing in from the sides. 

In conclusion, our reaction-diffusion model successfully captures pattern formation in this system on experimental length and time scales, with numerical simulations showing moving fronts of adsorbed carbon monoxide and oxygen similar to those observed experimentally and at comparable speeds.

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