A new synchronization mechanism via Turing-like microscopic structures for CO oxidation on Pt(110)

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We discuss an alternative to the traditional gas-phase coupling approach in order to explain synchronized global oscillations in CO oxidation on Pt(110). We use a minimalist microscopic model which includes structural Pt surface reconstruction via front propagation, and large diffusion rates for CO. The synchronization mechanism is associated with the formation of a Turing-like structure of the substrate. By using large parallel microscopic simulations we derive a scaling laws which allow us to extrapolate to realistic diffusion rates, pattern size, and oscillation periods.

Oscillations appear in experiments of CO oxidation on Pt(110) in a very narrow parameter interval [1]. Additionally, it is also possible to observe pattern formation; about T \sim 500K a crossover exist from spirals and fronts at low T to standing waves and chemical turbulence at high T. Experiments using fast scanning tunneling microscopy and field ion microscopy have clearly shown that fast kinetic processes are typically accompanied by the appearance of microscopic structures [2,3,4].

Although the diffusion of CO is fast, it does not provide a synchronization mechanism for the global oscillations, it is thought that the mechanism for global synchronization is coupling via the gas-phase [5]. This mechanism has been used widely in classical reaction-diffusion (RD) models. However, experiments have shown that particle dynamics on surfaces can be highly correlated [6], something which is not taken into account in RD models. This leads to differences between RD and experiments which can only be removed by including phenomenological corrections. An alternative mechanism for global synchronization of oscillations has been suggested based on spontaneous phase nucleation [6,7]. This nucleation results in a random creation of dynamic defects and leads to global synchronization via stochastic resonance.

We present in this paper Monte Carlo (MC) simulations of a microscopic model for CO oxidation on Pt(110). We show that our model can produce global oscillations via a new mechanism showing microscopic structures without gas-phase coupling, coupling via stochastic resonance, or lateral interactions. The microscopic structures appear in the substrate, but they also support pattern formation in the adlayer on a mesoscopic length scale. In addition we provide a connection between these MC simulations and experimental results, via scaling laws.

MC simulations provide a systematic approach to include microscopic effects [8]. MC simulates directly the chemical reaction steps in a model, without averaging out particle correlations. Simulations of our model were performed by using a Cellular Automaton (CA) which has been shown to be equivalent to MC [9]. A limitation of MC simulations has been the inability to deal with experimental system sizes and realistic diffusion coefficients. However, by using large parallel simulations as described in [4] we can now estimate results for experimental conditions. Using this parallel code we are able to simulate system sizes of about 1 \mu m with diffusion coefficients of about 10^{-10} cm^2 sec^{-1}. This approaches experimental conditions closer than any other previous MC simulation. Experimental values are for system sizes 10^2 \mu m or more and diffusion coefficient 10^{-6} cm^2 sec^{-1}. There is a gap between experimental and simulated rate constants, but, as we can vary the system size and the diffusion rate over a large range, we can derive scaling laws, which we can use to extrapolate the behavior predicted by our model to realistic system sizes and diffusion rates.

O_{2} adsorbs dissociatively onto two nearest neighbor sites with rate constant (1 − y)s_{\chi} with \chi = \alpha,\beta, where \alpha denotes the 1 \times 2 phase and \beta denotes the unreconstructed 1 \times 1 phase of Pt(110) [1]. The experimental value for the ratio of the sticking coefficients of O_{2} on the two phases is s_{\alpha} : s_{\beta} \approx 0.5 : 1. CO is able to adsorb on a free surface site with rate constant y and it desorbs from the surface with rate constant k. Both reactions are independent of the surface phase to which the site belongs. In addition CO is able to diffuse via hopping onto a vacant nearest neighbor site with rate constant D. The CO+O→CO_{2} reaction occurs with rate constant R, when CO and O are nearest neighbors sites. CO_{2} desorbs immediately forming two vacant sites. The \alpha \rightarrow \beta surface phase transition is modeled as a front propagation with rate constant V. For two nearest neighbor surface sites in the state \alpha\beta the transition \alpha\beta \rightarrow \alpha\alpha (\alpha\beta \rightarrow \beta\beta) occurs if none (at least one) of these two sites is occupied by CO. Summarizing the above transition definitions written in
the more usual form of reaction equations gives:

\[
\begin{align*}
\text{CO}(g) + S^\chi & \rightleftharpoons \text{CO}(a), \\
\text{O}_2(g) + 2S^\alpha & \rightarrow 2\text{O}(a), \\
\text{O}_2(g) + 2S^\beta & \rightarrow 2\text{O}(a), \\
\text{CO}(a) + S^\chi & \rightarrow S^\chi + \text{CO}(a), \\
\text{CO}(a) + \text{O}(a) & \rightarrow \text{CO}_2(g) + 2S^\chi, \\
S^\alpha & \rightleftharpoons S^\beta,
\end{align*}
\]

where \( S \) stands for a vacant adsorption site, \( \chi \) stands for either \( \alpha \) or \( \beta \), and (a) and (g) for a particle adsorbed on the surface or in the gas phase, respectively. For additional details see Ref. [13]. Our simulations use special normalization of the rates: the adsorption rate for CO is related to the partial pressures by

\[
y = \frac{P_{\text{CO}}}{P_{\text{CO}} + P_{\text{O}_2}}. \tag{1}
\]

Comparing our rate constants with typical experimental values used in RD models [14, 15] we can estimate the unit of time in our simulation to be about \( t_0 \approx 10^{-2}\text{s} \). All our rate constants are expressed in that unit of time.

Lengths are expressed in units of the unit cell parameter \( a \). The diffusion rate \( D \) is related to the experimental diffusion coefficient \( D_A \) by \( D_A = a^2 D / z t_0 \), where \( z = 4 \) is the coordination number.

The quality of the oscillations as a function of \( y \) has a typical resonance form. Well-defined oscillations are found near \( y = 0.494 \). Under certain condition, which we discuss below, these oscillations are global. Moving away from \( y = 0.494 \) we see first that the synchronization decreases and then a disappearance of the oscillations. We restrict ourselves to \( y = 0.494 \) (for a fixed values \( k = 0.1 \) and \( V = 1 \)) in our simulations.

We have found that two situations are possible depending on the system size, the diffusion rate, and on the initial conditions (IC). If the system is small or the diffusion is fast we find global oscillations. If the diffusion is too slow for a given system size the IC become important. We can again have global oscillations or the formation of patterns in the form of moving fronts and spirals.

To illustrate the synchronization mechanism Fig. 1 shows global oscillations. When the system is covered almost fully by CO the \( \beta \) islands in the \( \alpha \) background grow (snapshots 1 and 2). When the size of the \( \beta \) islands is large enough the rate of adsorption of \( O_2 \) becomes larger than the adsorption of CO on the \( \beta \) zones (snapshots 3 and 4). At the same time the CO in the \( \alpha \) zones is converted to \( \text{CO}_2 \) near to the borders with the \( \beta \) zones (snapshot 4). When the total coverage of oxygen becomes larger than CO, then the direction of the island growth is reversed (snapshots 4, 5, and 6) and \( \alpha \) islands grow in the \( \beta \) background. When the size of the \( \beta \) zones is not large enough to keep the oxygen coverage larger than the CO coverage (snapshot 7), then both phases are become covered by CO, and the cycle start again (snapshot 8). The key point in this cycle is the existence of a critical size of the \( \beta \) islands where oxygen becomes more stable than CO and a critical size of \( \alpha \) islands where CO is more stable than oxygen. This corresponds to a phase transition produced by a varying size of these islands. This phase transition is driven by diffusion and the critical size of the islands depends on the diffusion rate as \( \sqrt{D} \).

We found that the most important feature of the structures of the substrate is the typical distance between the islands; i.e., the correlation length \( l_c \) of these structures. For \( l_c \) we use the distance to the first maximum in the radially averaged correlation function of the substrate. The shape of the islands self-organizes through successive oscillations so that they cover the whole system with same sized islands separated by similar distances and small differences in size are removed. We note that our simple model of surface reconstruction by border propaga-
When the diffusion is slow pattern formation can also occur as on the right of Fig. 2. The period of oscillations, $T$, is a function of diffusion rate $D$. Numerically we found that the relations $T(D) \sim D^\nu$ and $l_c(D) \sim D^\mu$ holds with $\nu = 0.4849 \pm 0.016$ and $\mu = 0.5069 \pm 0.01$. For large $D$ values a large system size is required to compute $l_c(D)$ precisely. For instance for $D = 8000$ we use $L = 8192$. Additionally large diffusion rates means that most of the time is spend moving particles; on 8000 diffusion steps only one chemical reaction happens. Also the simulation time increases because the oscillation period increases with $D$.

A relationship $T(D) \sim l_c(D) \sim D^{1/2}$ seems quite reasonable, as our model has fast diffusion. In fact the scaling law for $l_c$ is the consequence of scaling law for $T$. The width of the Turing structure oscillates on a length of order $l_c$ due to the phase propagation with rate $V$. The period is related to these by $l_c \sim V T$. If the velocity $V$ is constant, then $l_c \sim T$. Fig. 3 was computed for a fixed value of $V$. Using a larger value for the velocity parameter we can obtain larger correlation lengths $l_c$ and smaller periods $T$, but the scaling remains the same. We have found for the Turing-synchronized oscillations that the relation $T \sim V^{-1/2}$ also applies as in \cite{1,2,6,7,13}. So we have an important scaling law in form $T = c \sqrt{D/V}$, where $c \sim 10$. An estimate for the oscillation period for realistic diffusion rates $D_A \sim 10^{-6} \text{ cm}^2\text{sec}^{-1}$ we have $D \sim 10^8$. The experimental oscillations period is $\tau = t_0 T$ with $t_0 \sim 10^{-2}$ sec and $\tau = 10$ sec. The value $V$ predicted by our model for that value of $\tau$ is then of the order of $V \sim 10^2$.

We propose that the minimal condition to have global oscillations is that the diffusion length $\xi$ is at least of the order of the correlation length $l_c$: $\xi = l_c (\xi = \sqrt{D T})$ and...
$l_c = V T, \ c \sim 10\). Critical values for the diffusion rate and the correlation length are then

$$D = c^2 V^3, \ l_c = c^2 V^2. \ \ (2)$$

For $V = 1$ we get the order of the parameters used in Fig. 2 (left side), $D \sim 10^2$ and $l_c \sim 10^2$ where global oscillations are possible but infrequently.

Diffusion is a thermally activated process so we can compare our proposal, Eqs. (2), with the experimental crossover at $T \sim 500$; for lower temperatures where fronts and spirals appear, we have lower diffusion rates, $\xi < l_c$ and the synchronization mechanism is not stable and produces patterns similar to on the right of Fig. 2. On the other hand for large temperatures where standing waves and chemical turbulence appear, we have large diffusion rates, $\xi > l_c$, and we get better synchronization, as in Fig. 3. For $\xi = l_c$ we get the crossover, Eqs. (2) holds and we get the minimum criteria for synchronization, as in Fig. 2 on the left.

Using $V = 10^2$ in Eqs. (2) we get for the critical value of diffusion rate $D \sim 10^8$, which corresponds to the experimental value of $D_A \sim 10^{-6}\text{cm}^2\text{sec}^{-1}$. This confirms our crossover idea. For correlation length $l_c \sim 10^6$ (in units of cell parameter $a$) we have a size $\sim 10^2$ $\mu$m which is of the order of magnitude of the standing waves observed in experiments 13. Near crossover it is possible to interpret $V$ also as the velocity $v$ of the fronts and spirals. For $V = 10^2$ we have $v = aV/t_0 \sim 10^{-4}$ $\text{cm s}^{-1}$, in agreements with experiments 16.

To summarize we present in this paper a new mechanism for synchronization of global oscillations based on microscopic Turing-like structures in the reconstruction of the surface. In cases with incomplete synchronized oscillations the adlayer has a mesoscopic second characteristic length. This is the first actual demonstration of a double length scale. Scaling laws are analyzed to connect the model to experimental parameter values.

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