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Catalytic Oscillatory Oxidation of CO on Pt(110): on-off Control to Chaos *

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An improved mean-field model, which specially takes into account pair correlation, was proposed to describe catalytic oscillatory oxidation of CO on Pt(110). By applying on-off control strategies under different frequency, the chemical oscillator shows an abundance of periodic doubling processes, even chaos response, and the route to the chaos and out of the chaos were both identified as period-doubling through analysis of its Lyapunov exponent spectrum. These response results reveal that structure delay effect plays an important role to the complexity of this system.

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The oscillatory CO oxidation on Pt(110) exhibits a rich variety of nonlinear behaviour including complex temporal and spatial dynamical patterns, which has been studied in considerable detail both experimentally and theoretically.[1-3] Most of these nonlinear phenomena have been well understood except the occurrence of deterministic chaos. Although a three-variable model, developed by Ertl's group,[4-6] can successfully explain bistability, kinetic phase transitions and period oscillation, it fails to describe the chaotic behaviour.[4] More meticulous study concerning the degree of faceting[5] of the surface atoms was expected to hold responsibility to the complex dynamics. However, the faceting appears at lower temperature than the chaos does. The exact origin of the chaos is still unclear.

It is well-known that periodic forcing of an oscillator may result in a large variety of phenomena, ranging from harmonic to chaotic response. By studying the response of a system under external perturbations, one can penetrate some intrinsic proprieties. Eiswirth *et al.*[5,8,9] carried out experimental studies by feeding a sinusoid oxygen partial pressure as a perturbation. They observed many interesting behaviours including harmonic resonance, subharmonic and superharmonic entrainment, as well as quasiperiodic behaviour. Then Krischer *et al.*[10] did an excellent theoretical study of periodic driving system to reveal a complex bifurcation fine structure of the Anord's tongues. We notice that all of these studies adopted sinusoid-form modulation, and the amplitude is small. In this paper, we adopt another kind of driven method: on-off control to study the responses under different frequency modulations.

We first reconstructed a lattice-gas model considering the basic reaction steps, because the Ertl's model[4,5] was developed within the framework of a mean field-type continuum description, ignoring the important pair correlation of CO and O. Then we analysed behaviour of the model. The on-off control was applied to the partial pressure of CO gas feeding. The response behaviour were studied lastly.

The mechanism of the catalytic oxidation of CO has been well established as the Langmur-Hinshelwood (LH) process.[14] The reaction is regarded as only taking place between two adsorbed species CO and O, and the reaction rate is generally given as proportional to the fractional coverage of CO and O according to mass-action dependence.[4-6] However, it is not always proper, especially when complex spatiotemporal self-organisation behaviour occurs. Mean-field approximation generally does not count in particle–particle interactions, either pair interactions or long range ones. So we rewrite the set of equations using lattice-gas model[15,17] based on elementary steps listed in Table 1.

Table 1 . Elementary steps for adsorption, desorption and diffusion processes.

No.	Process	CO(ads.)	O(ads.)
1	$O_2\downarrow$	0	+
2	$O_2\downarrow, CO_2\uparrow$	−	+
3	$O_2\downarrow, 2CO_2\uparrow$	−	0
4	$CO\downarrow$	+	0
5	$CO\downarrow, CO_2\uparrow$	0	−
6	$CO\uparrow$	−	0
7	$CO\rightarrow$	0	0
8	$CO\rightarrow, CO_2\uparrow$	−	−

Notes: $\downarrow$: adsorption, $\uparrow$: desorption, $\rightarrow$: diffusion;
+: increasing, −: decreasing, 0: unchanged

These processes show different influence on CO-coverage c and O-coverage o which are listed in the last two columns of Table 1. For 1×1 square lattice, we can easily develop two ordinary partial equations to describe variables c and o. They are

$$\frac{dc}{dt} = -2(1-y)s_o[1-(1-c)^3] + ys_c(1-o)^4 - Dc(1-c^4)[1-(1-o)^3] - R_d c, \quad (1)$$

$$\frac{do}{dt} = 2(1-y)s_o(1-c)^3 - ys_c[1-(1-o)^4] - Dc(1-c^4)[1-(1-o)^3], \quad (2)$$

where s_c and s_o denote sticking coefficients of CO (gas) and O_2 (gas); $(1-y)$ and y stand for their fractional partial pressure; and D, R_d stand for diffusion and desorption coefficients, respectively. Some explanation of the equations was given in Ref. 17. These two equations can be used to explain the kinetic phase transition from reactive windows to CO

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poisoning state. To explain oscillatory behaviour, an adsorbate-driven $1 \times 2 - 1 \times 1$ structural phase transition must be employed:[4-6,10]

$$\frac{da}{dt} = \begin{cases} -k_t a, & c \le 0.2, \\ k_t(1-a), & c \ge 0.5, \\ k_t\left(\sum_{i=0}^{3} r_i c^i - a\right), & 0.2 < c < 0.5, \end{cases} \quad (3)$$

where, the parameter a denotes the fraction of 1×1 phase. The temperature-dependent coefficient k_t and the fitting constants of cubic-function $\{r_0, r_1, r_2, r_3\}$ are given in Ref. 10.

When increasing the partial pressure of CO with Eqs.(1)−(3), we found the system exhibits monstable state first, then loses its stability to oscillation, and finally gains its stability suddenly to the CO-poisoning state. While $D = 0$ and $R_d = 0.1$, the oscillation exhibits in range $0.372 < y < 0.423$. If $D \neq 0$, the diffusion effect shifts the oscillation window higher.

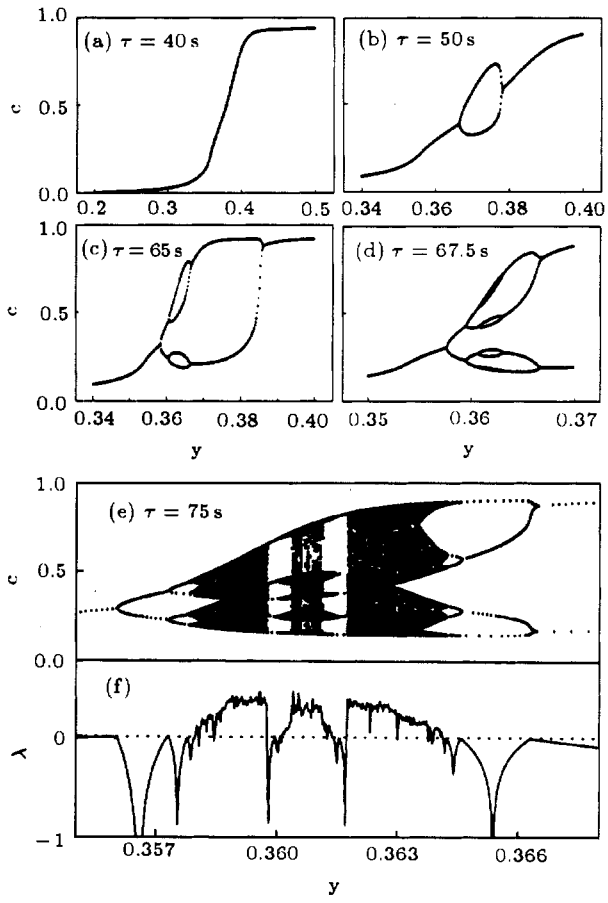

Fig. 1. Bifurcation scheme of the reaction model under different frequency of on-off control. Period doubling can be easily recognised from (a)−(e). As increasing partial pressure of CO, keeping on-off control frequency, (e) also exhibits period doubling process into and out of chaos; (f) is Lyapunov exponential spectrum of (e).

A surface catalytic reaction, generally, can be controlled by two ways. One can change the reaction conditions (pressure and temperature), or surface structure which results in changing of the distribution of active centres. On-off control[11] is one kind of control strategies applied to CO-feeding. Supposing the on-stage lasts a period τ_{on}, and then the off-stage lasts τ_{off}, let $\tau = \tau_{on} + \tau_{off}$, and the frequency $f = 1/\tau$. That is

$$y = \begin{cases} y, & t \in n\tau + \tau_{on}, \\ 0, & t \in n\tau - \tau_{on}, \end{cases} \quad n = 1, 2, 3, \cdots. \quad (4)$$

From numerical results of Eqs. (1)−(4), we found different bifurcation under different frequency control shown in Fig. 1 (keeping D=0.1 and R_d=0.03). When $f > 1/40$ Hz, no bifurcation appears [Fig. 1(a)], while f=1/50, 1/65, and 1/67.5 Hz, the system appears 2, 4, and 8-period bifurcation, respectively [Figs. 1(b)−(1d)]. After the frequency reaches a critical value $f_c \simeq 1/70$ Hz, the system may exhibit chaotic oscillation under proper y [Fig. 1(e)]. Figure 1(f) is Lyapunov exponent analysis of Fig. 1(e), where the chaotic oscillations appear while $\lambda > 0$. From Figs. 1(e) and 1(f), we obtained the route to chaos by period-doubling cascade (Feigenbaum route), and out of chaos by anti-Feigenbaum route.

These behaviours reveal an apparent delay effect of the structure transformation. The reconstruction of the surface atoms is a slower process comparing the reaction steps. At the short off-stage, the adsorbed CO is depleted quickly, but the 1×1-phase remains almost unchanged until on-stage comes. Therefore, the complex behaviour under different frequency control results from structure-delay effect. The similar chaos appearing in Pt(100)/NO+H_2 and Pt(100)/NO+CO systems has been confirmed also by structure delay-induced behaviour.[7]

In conclusion, we developed a model in which the pair correlation is included. The method traced back to the Monte Carlo simulation study with ZGB model.[15] By applying different frequency of on-off controls of CO-feeding, the system may exhibit a variety of behaviours ranging from stable state, 2-period, 4-period, $\cdots$, and finally to chaos. These response results reveal that structure-delay effect plays an important role in the system's dynamics, and further studies on the delay effect are expected to result in the final understanding of the chaos behaviour in autonomous system.

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