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Computer Simulation of the Transition to Chaotic Behaviour of Oscillations in the Rate of CO Oxidation on Pt(110)

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A model based on the coupling of two Sales–Turner–Maple (STM) mechanisms on a non-uniform surface has been found to be capable of describing the transition to chaotic behaviour of oscillations in the rate of CO oxidation on Pt(110).

There are two main approaches to the explanation of self-oscillations, based on ideas about the influence of the reaction medium on the surface properties. According to Ertl *et al.*,[1-3] self-oscillations in the CO oxidation rate result from phase transitions of the surface, induced by CO adsorption–desorption, for example (5 × 20)↔(1 × 1) on Pt(100). The second approach is based on the idea of the existence of oxygen adsorbed on the surface and near-surface (oxide) oxygen (the 'oxidation–reduction' model).[4-6]

Studies of the CO oxidation reaction on Pt(110) by LEED, XPS and TD methods[7-9] have shown that oscillations occur after a long induction period. During this period and further into the oscillation process, the surface structure and oxygen state change. Surface coverage with α_1-oxygen decreases, the amount of α_2-oxygen incorporated into the first layer increases, and a new form, subsurface β-oxygen, appears, *i.e.*, over time the reaction medium causes surface modification. The data obtained in refs. 7–9 allows us to consider the oscillation mechanism to be based on the oxidation–reduction model proposed by Sales, Turner and Maple (STM),[4-6] if we define 'oxide' oxygen as α_2-oxygen incorporated in the first surface layer.

Studies by Ertl *et al.*[10-12] on the CO oxidation reaction have established that as CO partial pressure decreases in the reaction mixture, doubling and redoubling (quadrupling) of the oscillation period occur with equal amplitude. This is followed by a transition to deterministic chaos, *i.e.* the order→chaos transition according to the Feigenbaum scenario. Analysis *via* the methods of non-linear dynamics[11] has made it possible to define the embedding dimension: $n = 5$ or 6 for different sets of experimental data, *i.e.* the minimum number of differential equations necessary to describe the system. However, neither a reaction scheme nor any corresponding mathematical model to describe these phenomena has appeared in the literature until now.

One may suppose that the surface is heterogeneous and consists of a 'chessboard' comprised of patches of two types which have similar properties and whose surface fractions are $M1$ and $M2$. On each of the $M1$ and $M2$ patches the reaction proceeds according to a five-stage mechanism (STM) with similar but not equal kinetic parameters. We have been interested in clarifying whether or not this model is able to describe any change in the period of oscillations.[10-12]

The reaction scheme may be recorded as shown in eqns. (1)–(11). In order to keep it short, there are no stages associated with β-oxygen formation and reduction in this scheme. Z_1 and Z_2 represent adsorption sites on patches $M1$ and $M2$.

$$O_2 + 2Z_1 \xrightarrow{k1_1} 2Z_1O\ (\alpha_1\text{-}O_{ads}) \qquad (1)$$

$$CO + Z_1 \overset{k1_2, k1_{-2}}{\rightleftharpoons} Z_1CO \qquad (2)$$

$$Z_1O + Z_1CO \xrightarrow{k1_3} CO_2 + 2Z_1 \qquad (3)$$

$$Z_1O \overset{k1_4, k1_{-4}}{\rightleftharpoons} Z_1O'\ (\alpha_2\text{-}O_{ads}) \qquad (4)$$

$$Z_1O' + Z_1CO \xrightarrow{k1_5} CO_2 + 2Z_1 \qquad (5)$$

$$O_2 + 2Z_2 \xrightarrow{k2_1} 2Z_2O(\alpha_1) \qquad (6)$$

$$CO + Z_2 \overset{k2_2, k2_{-2}}{\rightleftharpoons} Z_2CO \qquad (7)$$

$$Z_2O + Z_2CO \xrightarrow{k2_3} CO_2 + 2Z_2 \qquad (8)$$

$$Z_2O \overset{k2_4, k2_{-4}}{\rightleftharpoons} Z_2O'\ (\alpha_2\text{-}O) \qquad (9)$$

$$Z_2O' + Z_2CO \xrightarrow{k2_5} CO_2 + 2Z_2 \qquad (10)$$

$$Z_1CO + Z_2 \overset{k_{11}, k_{-11}}{\rightleftharpoons} Z_2CO + Z_1 \qquad (11)$$

A system of six kinetic differential equations may be derived [eqns. (12)–(17)].

$$[Z_1O]^\bullet = 2k1_1[Z_1]^1 - k1_3[Z_1O][Z_1CO] - k1_4[Z_1O] + k1_{-4}[Z_1O'] \qquad (12)$$

$$[Z_1CO]^\bullet = k1_2[Z_1] - k1_{-2}[Z_1CO] - k1_3[Z_1O][Z_1CO] - k1_5[Z_1O'][Z_1CO] + (k_{11}[Z_1CO][Z_2] - k_{-11}[Z_2CO][Z_1])\theta_L/M1 \qquad (13)$$

$$[Z_1O']^\bullet = k1_4[Z_1O] - k1_{-4}[Z_1O'] - k1_5[Z_1O'][Z_1CO] \qquad (14)$$

$$[Z_2O]^\bullet = 2k2_1[Z_2]^2 - k2_3[Z_2O][Z_2CO] - k2_4[Z_2O] + k2_{-4}[Z_2O'] \qquad (15)$$

$$[Z_2CO]^\bullet = k2_2[Z_2] - k2_{-2}[Z_2CO] - k2_3[Z_2O][Z_2CO] - k2_5[Z_2O'][Z_2CO] + (k_{11}[Z_1CO][Z_2] - k_{11}[Z_2CO][Z_1])\theta_L/M2 \qquad (16)$$

$$[Z_2O']^\bullet = k2_4[Z_2O] - k2_{-4}[Z_2O'] - k2_5[Z_2O'][Z_2CO] \qquad (17)$$

Material balance equations:

$$[Z_1] + [Z_1O] + [Z_1O'] + [Z_1CO] = 1.0 \qquad (18)$$

$$[Z_2] + [Z_2O] + [Z_2O'] + [Z_2CO] = 1.0 \qquad (19)$$

Reaction rate on $M1$:

$$R(M1) = (k1_3[Z_1O][Z_1CO] + k1_5[Z_1O'][Z_1CO])N_0.$$

Reaction rate on $M2$:

$$R(M2) = (k2_3[Z_2O][Z_2CO] + k2_5[Z_2O'][Z_2CO])N_0;$$

where N_0 is the number of centres per cm^2 of surface, $N_0 = 1.0 \times 10^{15}$ cm^{-2}.

Overall reaction rate $R_\Sigma = R(M1)M1 + R(M2)M2$.

Calculations have been performed for the case where $M1 = M2 = 0.5$. the fraction of boundary atoms *via* which CO_{ads} diffuses has been assumed to be $\theta_L = 1 \times 10^{-4}$. In the chessboard model this coincides with sections of size ≈ 5 micron. For 'white' patches the kinetic parameters for stages (1)–(5) are approximately the same as those in ref. 9, *i.e.*, $E_{-2} = 115$, $E_3 = 93$, $E_4 = 117.5$, $E_{-4} = 126$, $E_5 = 125$ kJ mol^{-1}. In all cases the preexponential factor has been assumed to be $\nu = 10^{13}$ s^{-1}. Sticking probabilities are as follows: for oxygen $s(O_2) = 0.3$, for carbon oxide $s(CO) = 1.0$. In assuming the surface to have only weak heterogeneity, we have changed only the constant E_2 to 114 kJ mol^{-1} for the 'black' patches ($M2$). The activation energies E_{11}, E_{-11} for diffusion were assumed to be ⩾ 80 kJ mol^{-1}. It should be noted that the activation energy for diffusion of CO_{ads} across a homogeneous platinum surface is about 40 kJ mol^{-1},[13] therefore the transition of CO_{ads} across patch boundaries is the rate-limiting step for its diffusion.

Integration of the system of differential equations (12)–(17) was carried out on an EC-1840 computer by the Rosenbrocke method.

Fig. 1(*a*–*c*) exhibits the computer-simulated time dependence

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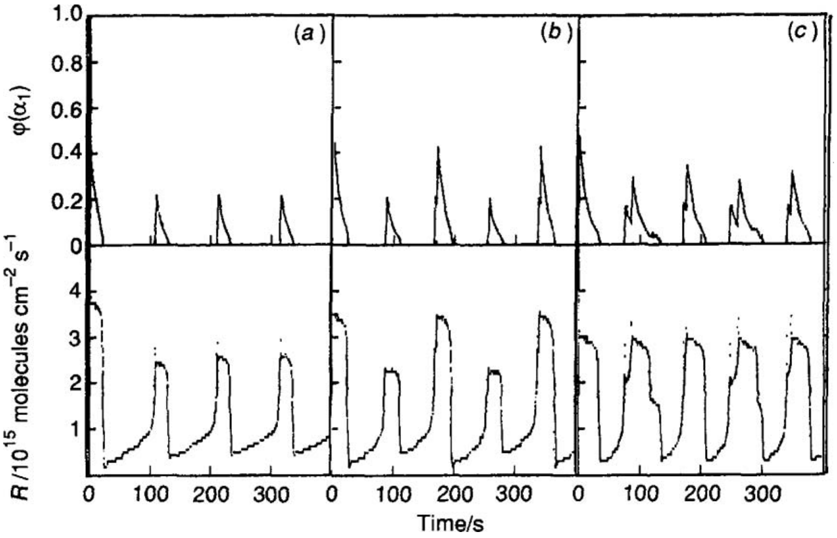

Fig. 1 Time dependence of the rate (lower part of the Figure) and of the coverage of the surface with α_1-oxygen [$\varphi(\alpha_1)$] (upper part) at $T = 450$ K; $P(O_2) = 4.0 \times 10^{-5}$ Torr and $P(CO) = 9.4 \times 10^{-6}$ (*a*), 9.0×10^{-6} (*b*) and 8.35×10^{-6} Torr (*c*). The diffusion activation energies are $E_{11} = 87$, $E_{-11} = 86$ kJ mol^{-1}.

of both the reaction rate and the surface coverage with α_1-oxygen: $\theta(\alpha_1) = [Z_1O]M1 + [Z_2O]M2$. The $\theta(\alpha_1)$ curves simulate the change of work function. These are given in order to facilitate comparison with the experimental data,[10–12] as in these works the reaction rate has been evaluated by surface potential measurements (Kelvin method).

With a relatively high CO pressure in the reaction mixture, $P(CO) = 9.4 \times 10^{-6}$ Torr [Fig. 1(*a*)],† single regular oscillations are observed, these oscillations occurring only on *M*2 patches. The *M*1 patches are covered with CO_{ads} and, due to CO_{ads} diffusion only, they 'feel' a drastic drop in coverage of CO_{ads} on the *M*2 patches at the reaction rate maximum. This leads to a slight decrease in coverage of CO_{ads} and to some increase of the rate on *M*1. In this case the *M*2 patches are 'leading' and the *M*1 patches are 'driven'. On decreasing the CO pressure to 9.0×10^{-6} Torr [Fig. 1(*b*)], the period of oscillations with the same amplitude doubles. In this case on *M*1 patches the situation is changed: 'leading-driven' oscillations (as for previous case) alternate with 'proper' oscillations. The decrease of $P(CO)$ to 8.35×10^{-6} Torr [Fig. 1(*c*)] results in a more complicated periodicity of oscillations.

On the whole the picture obtained [Fig. 1(*a*–*c*)] corresponds qualitatively to that observed experimentally by Ertl *et al.*[10–12] While analysing our model, we found that we could trace all the changes in the character of the oscillations in more detail by changing the diffusion rate of CO_{ads} at constant values of $P(CO)$, $P(O_2)$ and *T*.

At $E_{11} \leq 85$ kJ mol^{-1} complete synchronization occurs, and simple oscillations take place [Fig. 2(*a*)]. At $E_{11} = 87$ kJ mol^{-1} [Fig. 2(*b*)] the doubling of the oscillation period occurs and at $E_{11} = 89$ kJ mol^{-1} [Fig. 2(*c*)] we obtain a new doubling (quadrupling) of the period of oscillations with the same amplitude. Fig. 2(*d*) presents oscillations that are close to quasi-chaos. They arise when CO_{ads} diffusion is excluded between patches ($E_{11} = 190$ kJ mol^{-1}). The case of joint work of two surface patches which are not coupled by diffusion has been considered in refs. 14 and 15. By increasing E_{11} to > 90 kJ mol^{-1} we observe a transient regime of oscillations from Fig. 2(*c*) to Fig. 2(*d*). As an example, Fig. 3 demonstrates reaction rate and $\varphi(\alpha_1)$ curves calculated at 91 kJ mol^{-1}.

It should be noted that time dependences analogous to those above have also been obtained for other constants for patches

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† Torr = (101325/760) Pa.

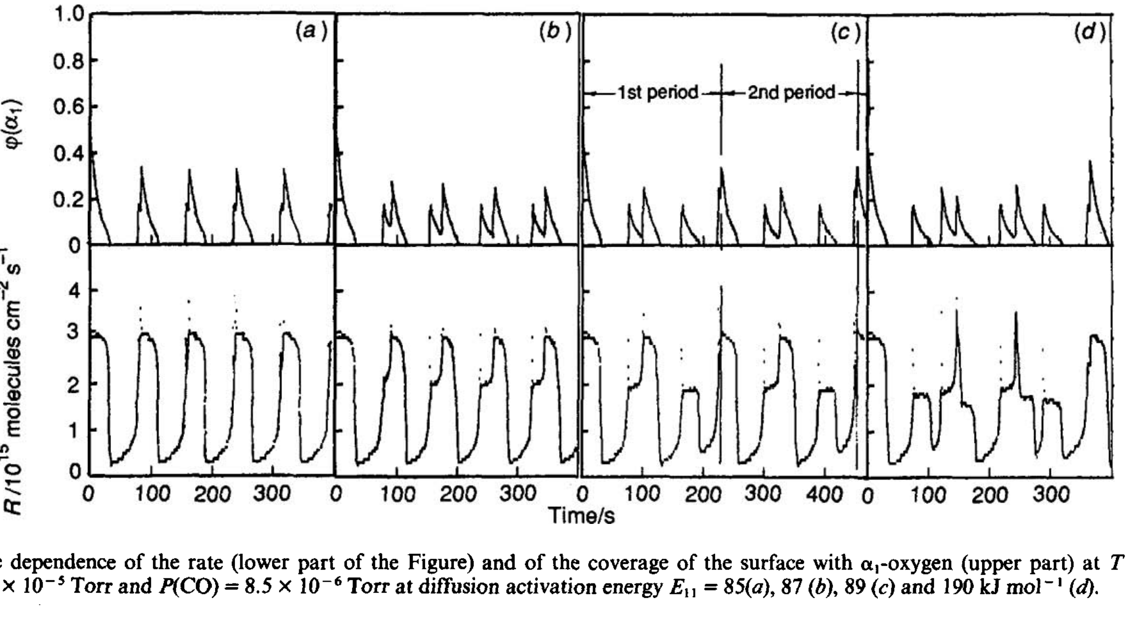

Fig. 2 Time dependence of the rate (lower part of the Figure) and of the coverage of the surface with α_1-oxygen (upper part) at $T = 450$ K; $P(O_2) = 4.0 \times 10^{-5}$ Torr and $P(CO) = 8.5 \times 10^{-6}$ Torr at diffusion activation energy $E_{11} = 85$(*a*), 87 (*b*), 89 (*c*) and 190 kJ mol^{-1} (*d*).

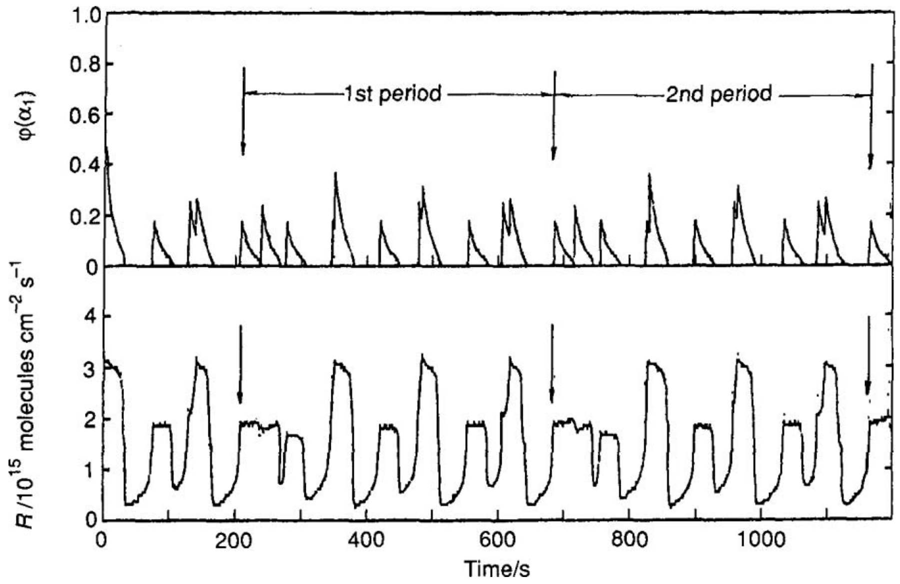

Fig. 3 Time dependence of the rate (lower part of the Figure) and of the coverage of the surface with α_1-oxygen (upper part) at $T = 450$ K; $P(O_2) = 4.0 \times 10^{-5}$ Torr and $P(CO) = 8.5 \times 10^{-6}$ Torr at diffusion activation energy $E_{11} = 91$ kJ mol^{-1}.

M2: $E_{-2} = 112$; $E_4 = 115$ kJ mol^{-1}.

Thus, our model, based on the coupling of two STM mechanisms, is capable of describing the order→chaos transition according to Feigenbaum. The mechanism of this model is quite simple. If two different oscillators are strongly coupled (high diffusion rate), then simple, regular oscillations take place. If they are not coupled [there is no diffusion, Fig. 2(*d*)], then each oscillator oscillates with its own frequency and, in summation, chaotic behaviour of the reaction rate becomes possible.[14,15] In the intermediate situation (moderate diffusion), transient regimes from simple, regular oscillations to deterministic chaos are possible.

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