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Two-variable periodic perturbation of kinetic oscillations

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Using one of the generic models (CO oxidation on Pt with surface-oxide formation) predicting kinetic oscillations in heterogeneous catalytic reactions, we show that the efficiency of two-variable periodic perturbations with respect to converting natural period-1 oscillations to period-l oscillations at the forcing frequency is remarkably sensitive to the kind of perturbations used. ''Counter-phase'' perturbations are much more effective compared to ''in-phase'' perturbations. The physics underlying these findings is suggestive of their applicability to many other models and/or real systems exhibiting kinetic oscillations.

KEY WORDS: heterogeneous catalysis; oscillatory reactions; periodic forcing; CO oxidation; surface oxide formation.

Periodic perturbations (or forcing) of oscillatory kinetics of chemical reactions in general [1–3] and heterogeneous catalytic reactions in particular [4–9] have long attracted attention. The results obtained in this field are related almost exclusively to perturbation of period-1 oscillations via periodic modulation of one governing parameter, e.g., of the incoming flux or pressure of one of the reactants or temperature (forcing of period-2 oscillations has recently been discussed in Ref. [9]). In real reactions, there are two or several reactants and accordingly one can simultaneously perturb two or more governing parameters. A general analysis of this situation was presented by Vance and Ross [10] in the case when oscillations occur near a Hopf bifurcation. What may happen in specific systems far from a Hopf bifurcation remains however to be explored. To address this problem, we present in this Letter the results of our study of forcing of kinetic oscillations generated in the framework of the famous oxide-formation mechanism proposed by Sales, Turner, and Maple[11] for CO oxidation on Pt-group metals (for a review of works related to this; model, see Ref. [12]).

According to the scheme under consideration, CO oxidation runs via the conventional catalytic steps, including reversible CO adsorption,

$$CO_{gas} \rightleftharpoons CO_{ads}, \tag{1}$$

irreversible dissociative O_2 adsorption,

$$(O_2)_{gas} \rightarrow 2O_{ads}, \tag{2}$$

and Langmuir–Hinshelwood (LH) reaction between adsorbed CO and O,

$$CO_{ads} + O_{ads} \rightarrow (CO_2)_{gas}, \tag{3}$$

combined with surface oxide formation,

$$O_{ads} \rightarrow O^*_{ads}, \tag{4}$$

and removal,

$$CO_{ads} + O^*_{ads} \rightarrow (CO_2)_{gas}, \tag{5}$$

where O^* is the oxide form of oxygen.

The simplest MF equations corresponding to the scheme above are as follows

$$d\theta_{CO}/dt = k_1 P_{CO}(1 - \theta_{CO} - \theta_O - \theta_{O^*}) - k_2\theta_{CO} - k_3\theta_{CO}\theta_O - k_{red}\theta_{CO}\theta_{O^*}, \tag{6}$$

$$d\theta_O/dt = 2k_4 P_{O_2}(1 - \theta_{CO} - \theta_O - \theta_{O^*})^2 - k_3\theta_{CO}\theta_O - k_{ox}\theta_O, \tag{7}$$

$$d\theta_{O^*}/dt = k_{ox}\theta_O - k_{red}\theta_{CO}\theta_{O^*}, \tag{8}$$

where θ_{CO}, θ_O, and θ_{O^*} are the adsorbate coverages, k_1, k_2, k_3, and k_4 the rate constants for CO adsorption, CO desorption, LH reaction, and O_2 adsorption, and k_{ox} and k_{red} the rate constants related to oxidation and reduction-of the cata1yst surface, respectively.

Perturbations of the reaction kinetics are assumed to result from variation of the reactant pressures,

$$P_{CO} = \langle P_{CO}\rangle[1 + A\cos(\omega t)], \tag{9}$$

$$P_{O_2} = \langle P_{O_2}\rangle[1 + B\cos(\omega t + \varphi)], \tag{10}$$

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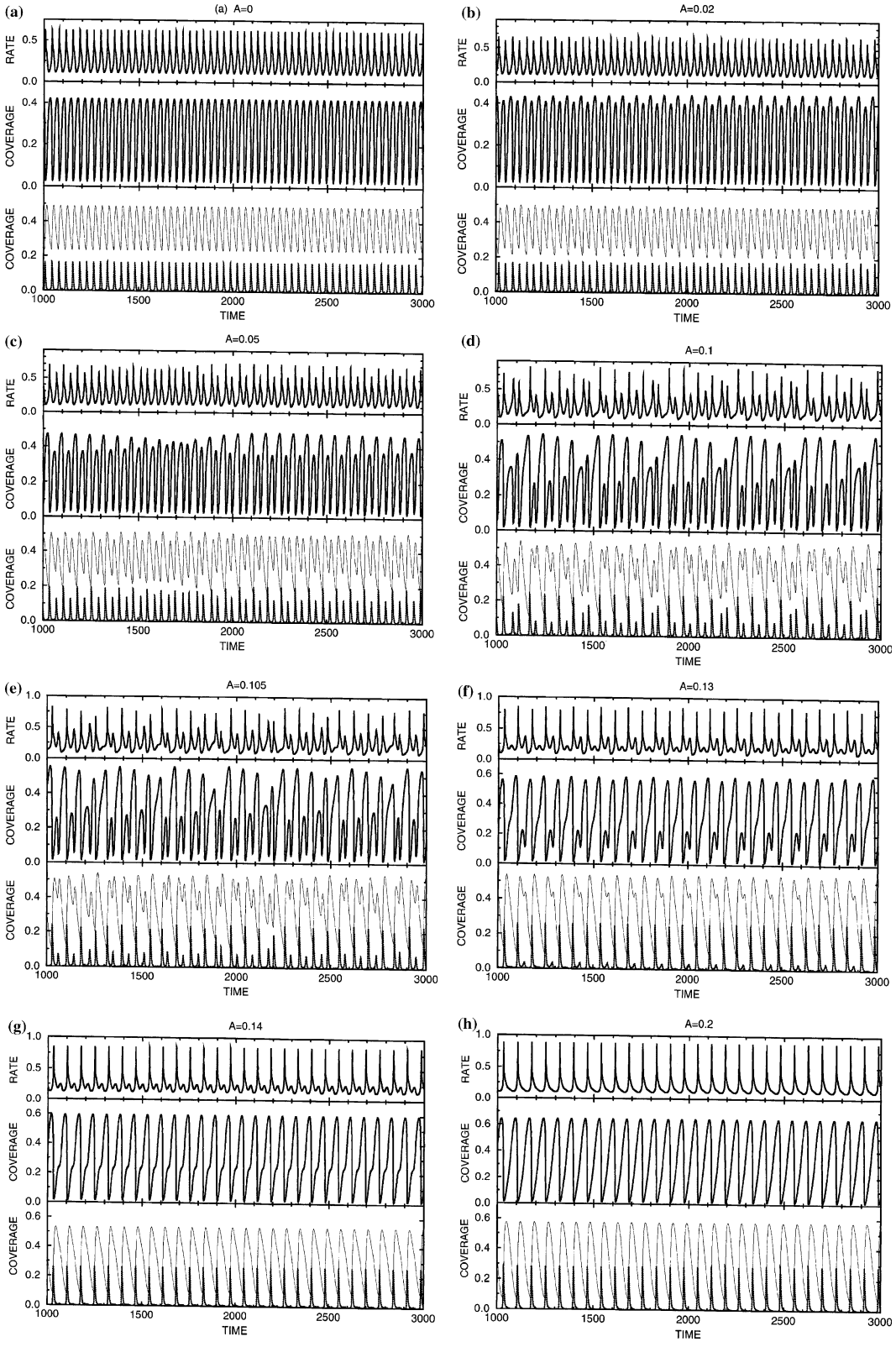

Figure 1. CO, O and O* coverages (thick solid, dotted, and thin solid lines, respectively) and the rate of CO_2 formation, $W = k_3\theta_{CO}\theta_O + k_{red}\theta_{CO}\theta_O{}^*$, as a function of time for perturbations of type (i) ($B = 0$) with $\omega/\omega_0 = 0.5$: (a) natural oscillations, (b) period-2 oscillations, (c) period-2 oscillations modulated with the period 18 times longer than the imposed period, (d) irregular oscillations, (e) period-4 oscillations, (f) period-2 oscillations, (g) and (h) period-l oscillations with the forcing frequency (this classification is based on the behaviour of coverages).

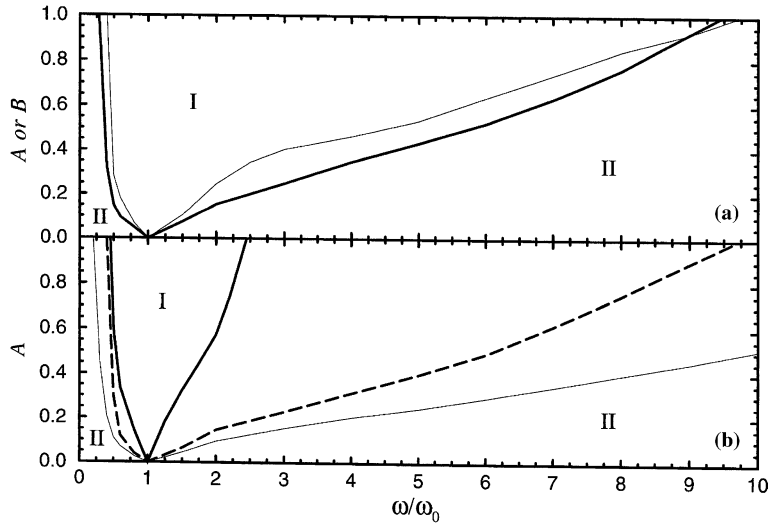

Figure 2. Kinetic phase diagrams showing the peninsulas of full entrainment (I) in the sea of other regimes (II): (a) for perturbations of type (i) with $A \neq 0$ and $B = 0$ (thick solid line) and type (ii) with $A = 0$, $B \neq 0$ and $\varphi = 0$ (thin solid line); (b) for perturbations of type (iii) with $A = B$ and $\varphi = 0$ (thick solid line), type (iv) with $A = B$ and $\varphi = -\pi/2$ (dashed line), and type (v) with $A = B$ and $\varphi = \pi$ (thin solid line).

where $\langle P_{CO} \rangle$ and $\langle P_{O_2} \rangle$ are the mean pressures, and ω, A, B and φ the forcing frequency, amplitudes, and phase, respectively. Specifically, we have analyzed five types of perturbations related, respectively, to (i) CO pressure ($A \neq 0$ and $B = 0$), (ii) oxygen pressure ($A = 0$ and $B \neq 0$), and both pressures including (iii) the "in-phase" regime ($A = B$ and $\varphi = 0$), (iv) "out-of-phase" regime ($A = B$ and $\varphi = -\pi/2$), and (v) "counter-phase" regime ($A = B$ and $\varphi = \pi$).

Equations (6)–(8) are known to predict oscillations provided that the LH step (3) is to oxide formation and removal steps ((4) and (5)). Guided by these prescriptions, we use for our calculations the following set of kinetic parameters: $k_1\langle P_{CO} \rangle = 0.9$, $k_2 = 0.2$, $k_3 = 100$, $k_4\langle P_{O_2} \rangle = 1$, $k_{ox} = 0.3$, and $k_{red} = 0.1$ (for convenience, we normalize all the reaction. rate constants to $k_4\langle P_{O_2} \rangle$ and employ the corresponding dimensionless time). With these parameters, the unperturbed model exhibits a stable well-developed limit circle (figure l(a)) with period $T_0 = 36.0$. (For similar MC kinetics, see Ref. [12].)

Concerning perturbations of the oscillations, it is appropriate first to recall that to some extent the behaviour of periodically perturbed oscillatory systems is universal [3]. With low-amplitude forcing, such systems usually exhibit a sea of quasi-periodic oscillations. Amongst this sea, are embedded a number of islands ("Arnold tongues") of periodic evolution corresponding to phase locking in the cases when the ratio of the forcing and natural frequencies, ω/ω_0, is close to an integer or simple fraction (in practice, one can usually track only the main tongues). With increasing amplitude of perturbations, one, may sometimes observe regular oscillations, modulated with the period appreciably exceeding the natural and imposed periods, or chaotic oscillations. As usual, the transition to chaos occurs via period doubling. The forcing with larger amplitude results eventually in full entrainment, i.e., in period-l oscillations with the imposed frequency. The model under consideration illustrates all these features as briefly shown in figure 1.

To characterize the effect of various perturbations on the oscillations or, more specifically, the efficiency of perturbations with respect to conversion of natural oscillations to period-l oscillations with the imposed frequency, We have constructed five kinetic phase diagrams (figure 2) showing the forcing amplitudes and frequencies corresponding to the onset of full entrainment (a full scale classification of the phase diagrams including Arnold tongues is beyond our present goals). The results obtained indicate that the perturbations of type (i) are slightly more efficient than those of type (ii) [figure 2(a)]. The effect of type-(iii) perturbations on oscillations is much weaker [in this case, the peninsula of full entrainment is very narrow (figure 2(b))]. For type-(iv) perturbations, the phase diagram nearly coincides with that corresponding to perturbations of type (i) [cf. figure2 (a) and (b)]. The highest efficiency is exhibited by perturbations of type (v). In the latter case, the boundaries of the full-entrainment region are located much lower than in all other cases [figure 2(b)].

Physically, the highest and lowest sensitivity of oscillations to respectively the "counter-phase" [type (v)] and "in-phase" [type (iii)] perturbations can be explained if one takes into account that in the case of unperturbed kinetics the oscillatory window (in the space of governing parameters) is usually relatively narrow (for the model under consideration, for example, the well-developed oscillations are observed at $0.7 \leq k_1\langle P_{co} \rangle \leq 1$ provided that the other parameters are fixed as indicated above). The "in-phase" perturbations correspond primarily to the motion inside the oscillatory

window and accordingly the stability of natural oscillations with respect to such perturbations is relatively high. In contrast, the "counter-phase" perturbations can easily shift the system outside the oscillatory window and accordingly convert natural oscillations to period-l oscillations with the imposed frequency.

In summary, using the Sales–Turner–Maple model, we have shown that the stability of natural oscillations with respect to periodic two-variable perturbations is remarkably sensitive to the type of perturbations. Specifically, the "counter-phase" perturbations easily convert natural oscillations to period-l oscillations with the imposed frequency. On the other hand, the "in-phase" perturbations are much less efficient. Finally, it is appropriate to note that the applicability of the model under consideration to real systems may be limited (see discussion in Refs. [13,14]). Qualitative explanation of the physics behind our findings indicates however that our general conclusions may be applicable to many other models and/or real systems exhibiting kinetic oscillations.

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