Periodic and random perturbation of catalytic oxidation of CO *

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Abstract When a controllable input is modulated by noise and signal, the response of a nonlinear system may exhibit a synchronized effect, which is referred to as stochastic resonance(SR). With the help of noise, the detection of weak signal may become possible and its signal-to-noise ratio can be increased. A model to describe catalytic oxidation of CO on single crystal was adopted, and its stability was studied by linear analysis method. Through computer simulation, the responses under periodic and random perturbation were analyzed. Stochastic resonance behavior was found in a narrow bistable region, or near the oscillatory region. The results shows more characteristics than those of 1-dimensional system does.

Keywords: **stochastic resonance, catalytic oxidation of CO, nonlinear dynamics, bifurcation.**

Noise always has a negative effect in linear systems. However, in some nonlinear systems, it may play a constructive role in detection of weak signals by increasing signal-to-noise ratio (SNR) through the mechanism known as stochastic resonance (SR). The concept of SR was originally put forward in the seminal papers by Benzi and his collaborators[1] wherein they addressed the problem of the periodically recurrent ice ages. The first experimental verification was obtained by Fauve and Heslot[2] in an electronic circuit known as a Schmitt trigger.

Recently, the concept of SR and its characteristics have been extended widely in physical and biological systems, and its application seems wide. In biology, SR had been recognized as the operating principle of sensory neurons to detect low frequency, weak signal, pointed out by Wiesenfel and Moss[3]; in physics, SR could be used as the mechanism to make physical sensory devices or used in communications; but no clue for chemistry. One of the basic requirements of SR is multistability. In addition, most of chemical reactions, either homogenous or heterogeneous, proceeding far from equilibrium, have rich complex spatiotemporal self-organization including multistability, waves, oscillations even chaos. Therefore, an abundance of SR behavior is expected there. In fact, some experimental results have been reported for SR in homogenous systems by Schneider's group[4—8]. In this paper, we focuse on a typical heterogeneous model, Pt(110)/$CO + O_2$, analyze its stability, and investigate the behavior and conditions of SR.

1 The reaction model

The catalytic oxidation of CO on Pt(110) follows Langmur-Hinshelwood (LH) mechanism. The basic steps include adsorption, desorption, reaction and diffusion, as well as an adsorb-driven phase transition of the surface atoms. Considering these basic steps, Krishcher, Eiswirth and Ertl[9—11]

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proposed a 3-variable model to describe the evolution of coverage of CO (u) and O (v), as well as the fraction of 1 × 1 phase (w). They are

$$\dot{u} = k_u P_u S_u\left[1 - \left(\frac{u}{u_s}\right)^3\right] - k_2 u - k_3 uv - D_{\text{eff}}, \tag{1}$$

$$\dot{v} = k_v P_v S_v\left[1 - \frac{u}{u_s} - \frac{v}{v_s}\right]^2 - k_3 uv - D_{\text{eff}}, \tag{2}$$

$$\dot{w} = \begin{cases} -k_5 w, & u \leqslant u_1, \\ k_5\left(\sum_{i=0}^{3} r_i u^i - w\right), & u_1 < u < u_2, \\ k_5(1 - w), & u \geqslant u_2, \end{cases} \tag{3}$$

where u_s and v_s stand for saturation coverage of CO and O; k_u and k_v for their sticking constants; the constants k_2, k_3 and k_5 are coefficients of desorption, reaction, and phase transition, respectively, related to temperature by Arrhenius rules, S_u and S_v are sticking coefficients for CO and O; let S_u = 1, $S_v = 0.6w + 0.4(1 - w)$. The cubic-fitting constants r_0, r_1, r_2, r_3 and all the others have been given in refs. [10,11]. The term D_{eff} was ignored because its effect does not cause any new kinetic behavior[5].

To obtain detailed proprieties of the model, one can apply linear stability analysis method to eqs. (1)—(3). The fixed points locate at $\dot{u} = 0$, $\dot{v} = 0$, and $\dot{w} = 0$. Let $\dot{u} = h(u, v(u, w))$, $\dot{w} = g(u, w)$. After linearization of eqs. (1)—(3), an eigenvalue equation is obtained for the fixed point P_0, i.e.

$$\begin{vmatrix} (\partial h/\partial u)_{P_0} - \lambda & (\partial h/\partial w)_{P_0} \\ (\partial g/\partial u)_{P_0} & (\partial g/\partial w)_{P_0} - \lambda \end{vmatrix} = 0. \tag{4}$$

The fixed points can be classified into stable/unstable nodes (n), stable/unstable foci (f), and saddle points (s) by their characteristic values.

2 Stochastic resonance in a narrow bistable region

The three basic ingredients of SR are (i) a weak coherent input signal, (ii) source of noise that is inherent in the system, and (iii) a nonlinear system with multistability. The signal and noise modulate the input of the nonlinear system, and the response information can be obtained by detecting the output correlation. SR refers that there is a peak on the curve SNR when the intensity of noise increases.

The simplest signal is sinusoidal wave, the popular noise is Gauss white noise, and the common analysis method of time series is power spectrum. For Pt(110)/CO + O_2, all the controllable parameters are (P_u, P_v, T); all the state variables are (u, v, w), or ratio of CO_2 production. Here, we kept $P_v = 1.3 \times 10^{-2}$ Pa unchanged, modulated P_u by a signal (amplitude A and frequency f_s) and noise(intensity D), and adopted CO-coverage as

$$P_u = P_{u0}[1 + A\sin(2\pi f_s t) + D\xi(t)], \tag{5}$$

where P_{u0} is a constant flow rate. The kinetics has been studied experimentally and theoretically under only periodic modulation[11—13]. Our special interest here is to study the synchronized effect of the signal and the noise.

While $T = 539$ K, $P_v = 1.3 \times 10^{-2}$ Pa, the bifurcation is plotted in fig. 1(a). A narrow bistable region is within $P_u = (36 \pm 0.25) \times 10^{-4}$ Pa. Determined by the initial state, the system may tend to the final state $u \approx 0.32$, the high state, or $u \approx 0.69$, the low state. We found that no transition occurs if the modulation amplitude is within $\pm 0.69\%$, else apparent hysteresis appears. From fig. 1(a), the low state jumps to the high state at point A as P_u increases, but the high state drops from sn_1 to point G while P_u decreases.

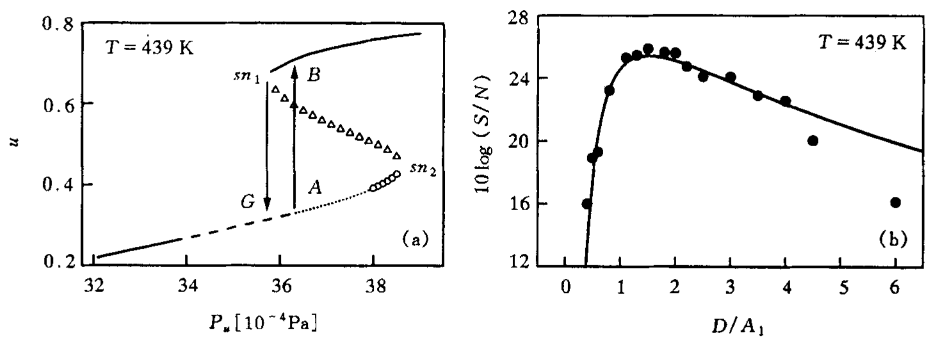

Fig. 1. Bistability of eqs. (1)—(3) for $T = 539$ K (a) and signal-to-noise curve as a function of noise intensity (b). The legends adopted in (a) are the solid line/open circle for stable/unstable nodes; the dashed/dotted line for stable/unstable foci, the open up-triangle for saddle points. The black dots in (b) are the simulation results guided by the solid line which is drawn with formula (6).

Set $P_{u0} = 36.00 \times 10^{-4}$ Pa, apply a weak signal with amplitude $A_1 = 0.2$ and frequency $f_s = 0.1$ Hz, no transition occurs due to the modulated P_u keeping within bistable region. The system's response to the periodic modulation is quite weak either for the low state or for the high state. Then, let the signal add to Gauss noise background. As the intensity of noise increases, transitions between the two states begin, and may become synchronic to the external signal gradually, which refers to the occurrence of SR. But too strong noise makes the transitions irregular, and the signal was annihilated finally.

The signal-to-noise ratio is defined as the ratio of signal peak's height on power spectrum over noise background. By analysis of the response time series under different noise strengths, we obtained the $SNR \sim D$ curve in fig. 1(b). There is a peak at $D/A_1 = 1.5$, where the black dots were from computer simulation, the solid line is a fitting curve of a formula of

$$R = \frac{S}{N} = \lambda\left(\frac{A}{D}\right)^2 \exp\left(-\frac{2\Delta U}{D}\right), \tag{6}$$

where $\Delta U \approx D_{\max}$ stands for the height of potential barrier. This formula was given to one-dimensional bistable model, obtained from Fockker-Planck Equation under adiabatic approximation, and under the approximations of $D \ll 1$ and $A \ll 1$[14,15]. We obtained that the formula agrees better near SR peak than strong noise does due to the restriction of formula (6).

In addition, it should be emphasized that the bistability exists in a "narrow" region, because the sensibility to small modulation resulted from the width of bistable region, and real SR is referring to the "weak" signal. The reason to cause the bistable region to be narrow can be explained from fig. 1(a). While the low branch loses it stability, it jumps to the upper branch immediately because the limit cycles around the unstable foci cannot exist. In contrast, the transition does not occur until the system jumps to sn_2 in 1-dimension systems.

3 Stochastic resonance near the oscillatory region

Figure 2(a) is a bifurcation scheme for $T = 542$K. The oscillation begins at a continuos Hopf bifurcation h, gains its amplitude, disappears suddenly at sn_1 while the loop touches the upper branch. Then, even three fixed points coexist in a wide range, only the upper branch is stable. At $P_{u0} = 39.8 \times 10^{-4}$ Pa, a weak signal with $A_2 = 0.25$, $f_s = 0.1$ Hz. This signal is not strong enough to stimulate transitions. If noise is added at the same time, a similar SNR curve can be obtained (see fig. 2(b)). It is surprising that this fitting curve with formula (6) shares the same parameter λ, and shows the same potential height ($\Delta U = 1.5A_1 = 1.2A_2 = 0.3$), which reveals that the little temperature difference does not change the height of the potential energy barrier though the dynamics changes greatly which corresponds to the difference characteristic of the potential energy surface. In addition, our results agree with the rule that SR is determined by nonlinear system itself, little related with external conditions, such as amplitude and frequency of signal.

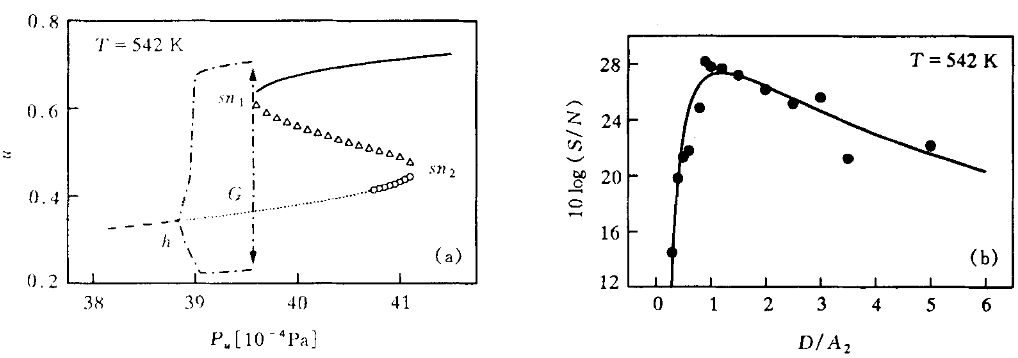

Fig. 2. Chemical oscillation of eqs. (1)—(3) for $T = 542$ K (a) and signal-to-noise curve as a function of noise intensity (b). The legends used here are the same as those in figure 1.

4 Conclusion

Stochastic resonance was found in bistable region and near the oscillatory region by simulating the catalytic oxidation of CO on Pt(110). Compared with one-dimensional bistability, the stochastic resonance in this narrow bistable region shows more sensitive to the external perturbation. The SR appearing near the oscillatory region, similar to one-threshold systems, reveals that coexistence of multistability is not a necessary condition. The key condition is that there is a discontinuous bifurcation.

Noise does not annihilate a weak signal, but plays a constructive role in the detection of weak signal. The benefit of noise suggests a new mechanism for us to produce chemical sensory devices.

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