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Theoretical Study on the Effects of Internal Noise for Rate Oscillations during CO Oxidation on Platinum(110) Surfaces

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Very recently, the effects of internal molecular noise in mesoscopic chemical reaction systems have gained growing attention. Using a mesoscopic stochastic model, the effect of internal noise for rate oscillation during CO oxidation on Pt(110) surface is studied analytically. In a parameter region outside but close to the supercritical Hopf bifurcation, a stochastic normal form is obtained from the chemical Langevin equation. By stochastic averaging procedure, the system is simplified and solvable. Noise-induced oscillation and internal noise coherent resonance (which is related to an optimal system size), observed from simulations, are well reproduced by the theory. The theoretical analysis helps to clearly figure out when and how the internal noise affects the system's oscillating dynamics.

1. Introduction

In the last two decades, the constructive roles of noise in nonlinear systems have gained much attention. The well-known phenomenon, stochastic resonance (SR), shows that there exists a "resonant" noise level where the response of a bistable system to a feeble external periodic signal is maximally ordered. Since it was put forward in the early 1980s,[1] SR has been studied in a variety of physical,[2] chemical,[3] and biological[4−8] systems. Recently, many SR-like behaviors have been reported in small-scale chemical or biological reaction systems, where the number of reactant molecules is often low and the internal noise, resulting from stochasticity of chemical reaction events, becomes considerable, and plays important roles. Specifically, for mesoscopic chemical reaction systems with oscillating dynamics, internal noise can induce stochastic oscillations in parameter regions where a corresponding macroscopic system does not show oscillation, and the noise-induced oscillation (NIO) shows the best performance at an optimal internal noise level. Compared to the original SR behavior in bistable systems, for this phenomenon, which is often called internal noise coherent resonance (INCR),[9] the noise is internal, which is inherent in mesoscopic chemical systems; the system's dynamics is oscillatory, and the external signal is absent. Because the magnitude of the internal noise is generally inversely proportional to the system size, INCR also implies the existence of an optimal system size. So far, many behaviors of this type have been found, for instance, in calcium-signaling process,[10] ion-channel-related process,[11−15] circadian oscillation systems,[16] surface catalytic reactions on single crystals or nanoparticles,[17−18] etc. However, most of these studies are only based on numerical simulations, and few analytical works were reported.

In a recent paper, we have performed an analytical study of the NIO and INCR behavior in the conceptual Brusselator model.[19] Observing the fact that many of the NIO and INCR behaviors were found in a parameter region close to supercritical Hopf bifurcation (HB), we believed that some common features of HB must be relevant. According to HB theory, the system's dynamics near the bifurcation point can be reduced to a normal form equation governing the evolution of a complex magnitude on the two-dimensional center manifold associated with the two conjugate eigenvalues of the Jacobi matrix of the vector field. Therefore, we start from the chemical Langevin equation (CLE) currently proved to be valid by Gillespie and obtain the stochastic normal form. After a "stochastic averaging procedure," a simplified stochastic normal form was finally obtained from which analytical expressions for the probability distribution function of the oscillation amplitude, the autocorrelation function and correlation time, and the signal-to-noise ratio (SNR) of the stochastic oscillation were all obtained. The theoretical results showed rather good agreement with the numerical simulation.

In the present paper, we will use the above analytical method to study the effect of internal noise in a surface catalytic system. The catalytic oxidation of carbon monoxide (CO) has attracted a lot of attention for more than two decades, due not only to its application, but also to its theoretical significance. At low pressures and typical temperatures, the surface can be regarded as locally well mixed, and simple mean field models in the form of deterministic reaction−diffusion equations have been very successful to reproduce many experimental observations. However, when looking at very small length scales, internal noises become crucial and must be considered. In heterogeneous catalysis, sufficiently small systems to be strongly influenced by internal noise are provided by the facets of a field-emitter tip,[20] by nanostructured composite surfaces,[21] and by the small metal particles of a supported catalyst.[22] Also, when the pressures are increased the size of a locally well-mixed cell would decrease to a small scale where a mean-field type of reaction−diffusion equations becomes less accurate and internal noises becomes important. For example, internal noise can induce transitions between the active and inactive branch of the reaction for catalytic CO oxidation on a Pt tip,[23] can lead to the large difference between the oscillations observed on 4 and 10 nm Pd particles,[22,24,25] and may be responsible for the bid

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TABLE 1: Reaction Steps and Corresponding Transition Rates Involved in the Model

process	descriptions	transition rates
$N_{CO} \rightarrow N_{CO} + 1$	CO adsorption	$a_1 = Np_{CO}\kappa_{CO}s_{CO}(1 - u^{\xi})$
$N_O \rightarrow N_O + 2$	O_2 adsorption	$a_2 = 1/2\ Np_{O_2}\kappa_O s_{CO}$ $[s_O{}^{1\times 2}(1 - w) + s_O{}^{1\times 1}w](1 - u)^2(1 - v)^2$
$N_{CO} \rightarrow N_{CO} - 1$	CO desorption	$a_3 = N[k_{des}^{1\times 2}(1 - w) + k_{des}^{1\times 1}w]u$
$N_{CO} \rightarrow N_{CO} - 1$ $N_O \rightarrow N_O - 1$	reaction	$a_4 = Nk_{re}uv$
$N_{1\times 1} \rightarrow N_{1\times 1} + 1$	(1 × 2) to (1 × 1)	$a_5 = Nk_{1\times 1}(1 - w) \times f_{1\times 2}(u,w)$ with $f_{1\times 1}(u, w) = (1 - \epsilon)u^{\lambda} + \epsilon w^{\lambda}$
$N_{1\times 1} \rightarrow N_{1\times 1} - 1$	(1 × 1) to (1 × 2)	$a_6 = Nk_{1\times 2}w \times f_{1\times 2}(u,w)$ with $f_{1\times 2}(u,w) = (1 - \epsilon)(1 - u)^{\lambda} + \epsilon(1 - w)^{\lambda}$

discrepancy between the experimental observations and theory in the study of spatiotemporal self-organization in catalytic oxidation of hydrogen on Pt(111).[26] Noteworthy, Mikhailov and co-workers have developed Langevin type reaction−diffusion equations to successfully describe the formation of "nonequilibrium nanostructures" in surface reaction systems by taking into account chemical reaction and diffusion as well as lateral physical interactions.[27] Herein, we will mainly focus on the effect of internal noise to rate oscillation during CO oxidation on Pt(110) single-crystal surface. Our study is mainly analytical, and numerical simulations are also performed to compare with the theory.

The motivation of this research is as follows. First, from this theoretical work one could get more insight into the mechanism of the effects of internal noise in surface catalytic systems and help one to figure out when the internal noise is critical and how its effects can be controlled externally. This would help us for more reasonable design of catalyst reactions. Second, the surface catalytic reaction is much more complex than the Brusselator, and we also want to further demonstrate the validity of our analytical method. The model and the problem are addressed in Section 2, we perform our analytical study in Section 3, comparisons between the theory and numerical results are present in Section 4, and we end by discussions in Section 5.

2. Model Description

The model we use in the present paper was developed to describe the temporal dynamics of catalytic oxidation of CO on low-index Pt(110) single-crystal surfaces.[28] This system has been extensively studied and the reaction was found to follow a Langmuir−Hinshelwood mechanism.

$$CO + * \rightarrow CO_{ad}$$

$$O_2 + 2* \rightarrow 2O_{ad}$$

$$CO_{ad} + O_{ad} \rightarrow CO_2 + 2*$$

Here, a vacant adsorption site is denoted by the asterisk (*), and an adsorbed species by the subscript "ad". To account for the rate oscillation, the adsorbate-induced phase transition 1 × 2 ⇔ 1 × 1 for Pt (110) surface must be taken into account to address the influence of the surface structure on the reactivity. We focus on a small "cell" on the surface containing N adsorption sites inside which the reaction is homogeneous. For instance, the small region of a field-emitter tip is about 20 × 200 Å^2 and contains 10^6 surface sites.[23] As stated above, the reactions inside this small space are stochastic, and one should use mesoscopic stochastic models to describe the dynamics. The state of the system is denoted by a vector $X_N(t) = [N_{CO}(t), N_O(t), N_{1\times 1}(t)]^T$, where N_{CO}, N_O, and $N_{1\times 1}$ denote the number of adsorbed CO molecules, adsorbed oxygen atoms, and adsorption sites in a nonreconstructed (1 × 1) phase, respectively. All these variables are stochastic, and the reaction steps leading to their changes are listed in Table 1. Note that the transition rates $a_{i = 1,...,6}$ are all proportional to the system size N, and we have introduced the concentrations $u = N_{CO}/N$, $v = N_O/N$, and $w = N_{1\times 1}/N$. One may turn to ref 28 for details of the parameter description and values.

From the processes in the above table, the chemical master equation for this system can be readily written down. Although the exact simulation algorithm that mimics the reaction dynamics by randomly determining what the next reaction is and when will it happen was proposed by Gillespie in 1977,[29] it is too time consuming when the system size is large. To overcome this difficulty, one may use Langevin type equations that describe the "Brownian motion" of the macroscopic concentration variable under the influence of microscopic stochastic interactions.[30] Recently, Gillespie stated that the CLE is a rather good approximation if a "macroinfinitesimal" time scale exists in the dynamics.[31] This condition may be satisfied if the total number of reactant molecules is not too small. In our previous studies,[16,32] we have shown that it is convenient to use CLE to study the influence of internal noise in mesoscopic reaction systems, at least qualitatively. According to Gillespie, the CLE for the current model reads

$$\begin{aligned} \frac{du}{dt} &= \frac{1}{N}[(a_1 - a_3 - a_4) + \sqrt{a_1}\,\xi_1(t) - \sqrt{a_3}\,\xi_3(t) - \sqrt{a_4}\,\xi_4(t)] \\ \frac{dv}{dt} &= \frac{1}{N}[(2a_2 - a_4) + 2\sqrt{a_2}\,\xi_2(t) - \sqrt{a_4}\xi_4(t)] \\ \frac{dw}{dt} &= \frac{1}{N}[(a_5 - a_6) + \sqrt{a_5}\,\xi_5(t) - \sqrt{a_6}\,\xi_6(t)] \end{aligned} \tag{1}$$

where $\xi_{i = 1,...,6}(t)$ are Gaussian white noises with $\langle\xi_i(t)\rangle = 0$ and $\langle\xi_i(t)\xi_j(t')\rangle = \delta_{ij}\delta(t - t')$. The items with $\xi_i(t)$ give the internal noises, which scale as $1/\sqrt{N}$ because $a_{i = 1,...,6} \propto N$. When $N \rightarrow \infty$, the internal noise items can be ignored and the system's dynamics is described by the deterministic equation

$$\frac{du}{dt} = \frac{1}{N}(a_1 - a_3 - a_4), \qquad \frac{dv}{dt} = \frac{1}{N}(2a_2 - a_4), \qquad \frac{dw}{dt} = \frac{1}{N}(a_5 - a_6) \tag{2}$$

As shown in Figure 2 of ref 28, the deterministic system shows very abundant bifurcation features in the control parameter space of p_{CO} and p_{O_2}. For example, if we fix $p_{O_2} = 9.6 \times 10^{-5}$ mbar, $T = 520$ K, and choose p_{CO} as the only control parameter, the system shows HB and excitability, which leads to an interesting phenomenon called Canard explosion.[33−35] In a recent paper, we have investigated the effects of internal noise

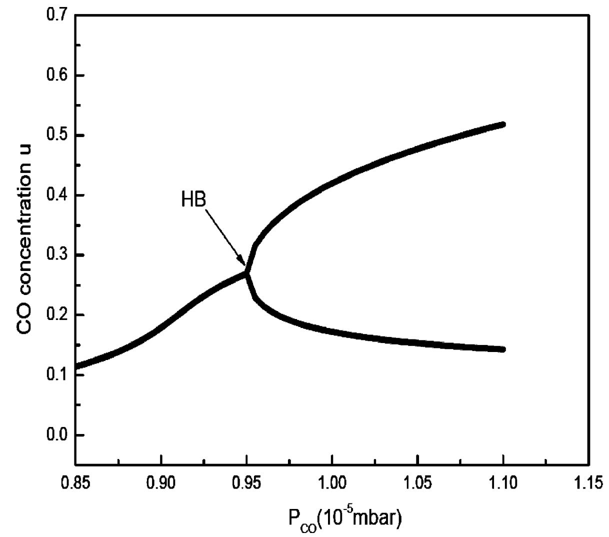

Figure 1. Bifurcation diagram for the deterministic system (eq 2), HB stands for the supercritical HB at $p_{CO} = 0.95022 \times 10^{-5}$ mbar.

for this parameter values numerically, and a kind of system size biresonance was found.[18] The double peaks in the SNR of the internal NIO were shown to be relevant to the Canard phenomenon. Because of the existence of Canard explosion, a theoretical analysis was hard to be made. In the present paper, we will mainly focus on the effect of noise near the HB. For simplicity, we fix $p_{O_2} = 2.0 \times 10^{-5}$ mbar, $T = 520$ K, and choose p_{CO} as the control parameter such that the HB is not accompanied by the Canard phenomenon. The bifurcation diagram of the deterministic system is shown in Figure 1, where a supercritical HB locates at $p_{CO}^{H} = 0.95022 \times 10^{-5}$ mbar. Our analysis is focused on the parameter region outside but close to the supercritical HB.

3. Theoretical Analysis

For convenience, we can write eq 1 in a more compact form:

$$\frac{dx_i(t)}{dt} = \sum_{\rho=1}^{6} \nu_{i\rho} a_\rho(\{x_i\}) + \frac{1}{\sqrt{N}} \sum_{\rho=1}^{6} \nu_{i\rho} \sqrt{a_\rho(\{x_i\})}\, \xi_\rho(t)$$

$$\equiv F_i(\{x_i\}) + \frac{1}{\sqrt{N}} \sum_{\rho=1}^{6} \nu_{i\rho} \sqrt{a_\rho(\{x_i\})}\, \xi_\rho(t) \qquad (3)$$

where ($x_1 = u$, $x_2 = v$, $x_3 = w$). $\nu_{i\rho}$ are the stoichiometric coefficients and in this system $\nu_{1\rho} = (1\ 0\ {-1}\ {-1}\ 0\ 0\ )$, $\nu_2 = (0\ 2\ 0\ {-1}\ 0\ 0)$, and $\nu_3 = (0\ 0\ 0\ 0\ 1\ {-1})$. According to the Hopf theorem,[36] the Jacobi matrix $(\mathbf{J})_{ij} = \delta F_i\ (\{x_i\})/\delta x_j$ has a pair of conjugate eigenvalues $\lambda_\pm = \alpha \pm i\omega$ for $p_{CO} \cong p_{CO}^{H}$, with $\alpha <$ 0(> 0) for $p_{CO} < p_{CO}^{H}$ ($> p_{CO}^{H}$). Then we carefully change the control parameter in this region, calculate the fixed point $\mathbf{x}_s = (u_s, v_s, w_s)$ and the eigenvalues $\lambda_\pm = \alpha \pm i\omega$ of the Jacobian matrix. The HB can be exactly located when α bypasses zero. NIO and coherent resonance are expected to happen to the left side of p_{CO}^{H}. As already stated, the dynamics near the HB can be described by a "normal form" equation on the center manifold.[36] Starting from the CLE (eq 3), a stochastic normal form equation can be obtained as the following:

$$\frac{dZ}{dt} = (\alpha + i\omega)Z + (C_r + iC_i)|Z|^2 Z + \frac{1}{\sqrt{V}} \sum{}_\rho (\tilde{\nu}_{1\rho} + i\tilde{\nu}_{2\rho}) \sqrt{a_\rho}\, \xi_\rho(t) \quad (4)$$

where C_r and C_i are constants determined by the nonlinear terms in $F_{i=1,2,3}(\{x_i\})$.

Here are some details associated with eq 4.[36] For a given p_{CO}, the fixed point $\mathbf{x}_s = (u_s, v_s, w_s)$ of eq 2, eigenvalues ($\lambda_\pm = \alpha \pm i\omega$, λ_3) and the corresponding eigenvectors ($\mathbf{u}_\pm$, $\mathbf{u}_3$) of the Jacobian matrix $(\mathbf{J})_{ij}$ can be calculated. Via normalization, we can set the first nonzero component of $\mathbf{u}_+$ to 1. Write the eigenvectors as $\mathbf{u}_\pm = \{1, a \pm ib, c \pm id\}$, $\mathbf{u}_3 = \{e, f, g\}$, the transformation matrix $\mathbb{T}$ has the form $\{(1, 0, e), (a, -b\ ,f), (c, -d, g)\}$ that meets the condition that $\mathbb{T}\mathbf{J}\mathbb{T}^{-1} = \{(\alpha, -\omega, 0), (\omega, \alpha, 0), (0, 0, \lambda_3)\}$. Perform the change of variables $\mathbf{x} = \mathbf{x}_s + \mathbb{T}\mathbf{y}$, where $\mathbf{y} = (y_1, y_2, y_3)$ is a new state vector, and the complex amplitude is $Z = y_1 + iy_2$. The coefficients $\tilde{\nu}_{1\rho}$ and $\tilde{\nu}_{2\rho}$ in eq 4 are obtained via $(\mathrm{T}\tilde{\boldsymbol{\nu}})_{\boldsymbol{i\rho}} = (\mathbb{T}^{-1}\nu)_{i\rho}$; C_r and C_i are calculated numerically, and the result is $C_r = -5.27897$, $C_i = 3.86874$ at p_{CO}^{H}.

By writing $Z = re^{i\theta}$, the time evolution of oscillation amplitude r and phase θ can be obtained. In the vicinity of the supercritical HB ($|\alpha| \ll 1$), the evolution of r is slow and that of θ is much faster. This time-scale separation makes it possible for the use of stochastic averaging procedure,[37] which can approximate the system as a Markov processes in the long time limit. Consequently, the following simplified Ito stochastic differential equations are obtained:

$$\frac{dr}{dt} = \left(\alpha r + C_r r^3 + \frac{\epsilon^2}{2Nr}\right) + \frac{\epsilon^2}{\sqrt{N}}\, \xi_r(t) \qquad (5a)$$

$$\frac{d\theta}{dt} = (\omega + C_i r^2) + \frac{\epsilon^2}{r\sqrt{N}}\, \xi_\theta(t) \qquad (5b)$$

where ξ_r and ξ_θ are two "new" Gaussian white noises. Generally, the reaction rates a_ρ can be expanded in the series in the form $a_\rho = \sum_{k+l=0}^{n} a_\rho^{(kl)}\ (r \cos\theta)^k\ (r \sin \theta)^l$. For small noise level, $r^2 \ll 1$, and it is a good approximation to neglect the terms with $k + l \geq 2$. We have $\epsilon^2 = \sum{}_\rho(\tilde{\mathrm{v}}_{1\rho}^2 + \tilde{\mathrm{v}}_{2\rho}^2)a_\rho^{(00)}/2$.

Note that even in the region subthreshold to the HB where $\mu < 0$ and the deterministic system (eq 2) does not show oscillation, one still can find nonzero solutions for $\alpha r + C_r r^3 + \epsilon^2/2Nr = 0$ in eq 5a, which is $r_s = [(\sqrt{\alpha^2 - 2C_r\epsilon^2/N} + \alpha)/(\ -2C_r)\}]^{1/2}$. Later, it will be shown that it corresponds to the most probable value of the amplitude of the NIO. In addition to a finite system size N, a nonzero $a_\rho^{(00)}$ is also necessary for r_s to have a nonzero value. The latter is always true for chemical reactions with nonzero steady-state concentrations $\mathbf{x}_s$.

In the literature, one often used the effective SNR to characterized the performance of the NIO.[32] Because the variable r is fully separated from θ in eqs 5a and 5b, an analytical expression for the SNR is available (see ref 19 for details). In this system, the stationary probability distribution function of r and auto-correlation function (ACF) for cos θ are given by

$$\rho_s(r) = C_0 r \exp\left(\frac{2\mu r^2 + C_r r^4}{2(\epsilon^2/N)}\right) \qquad (6a)$$

$$C_\theta(\tau) = \lim_{t\to\infty} \langle \cos\theta(t) \cos\theta(t+\tau)\rangle = \frac{1}{2}\cos(\omega_1 \tau) \exp(-\tau/\tau_c) \qquad (6b)$$

Here, C_0 is a normalization constant. It is easy to check that $p_s(r)$ has a single maximum at $r = r_s$; hence in the stationary state, the system will most likely stay around this limit cycle

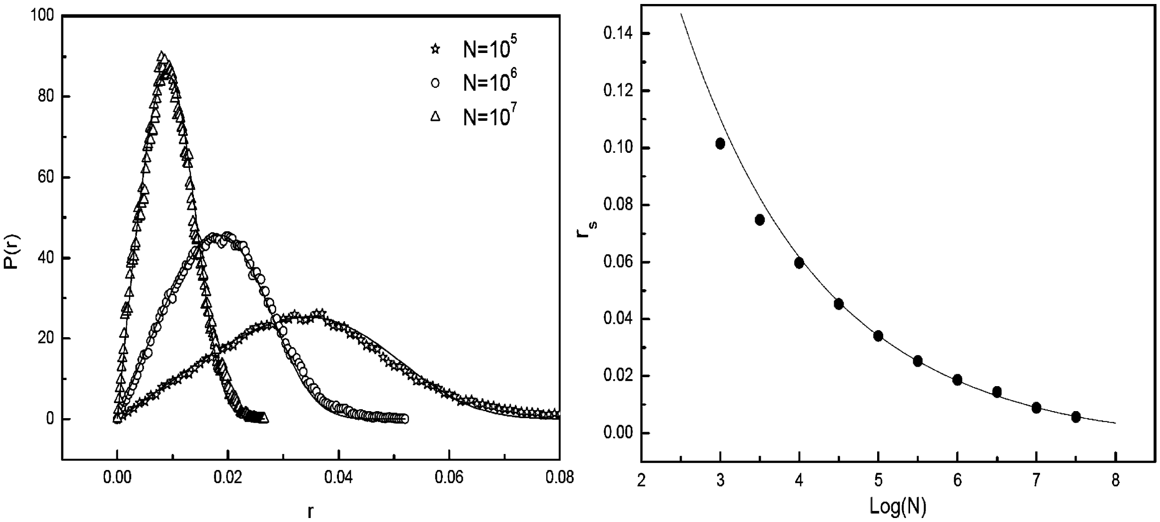

Figure 2. (a) Stationary distribution of $r(t)$ obtained from simulation (symbols) and theoretical eq 6a (lines). $\alpha = -0.00056$, $\log(N) = 5,6,7$. (b) Dependence of most probable values of $r(t)$ on the system size N from numerical calculations (circles) and analytical results (lines).

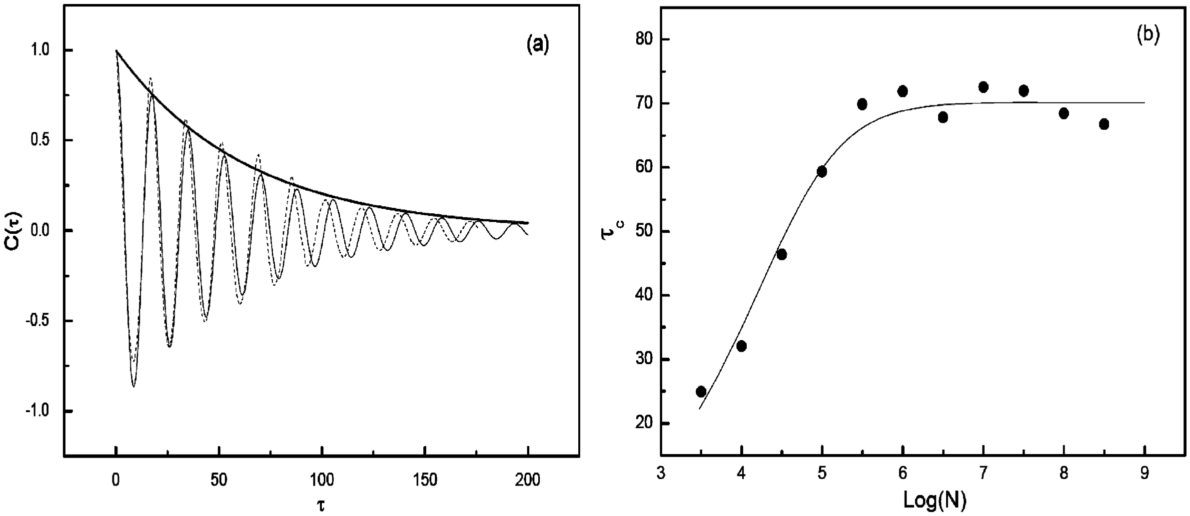

Figure 3. (a) A typical autocorrelation function obtained from the theoretical eq 6b (thin solid line) and numerical calculations (dashed line). Thick solid line is a fit using an exponential decay from which we can calculate approximately the autocorrelation time. $\alpha = -0.01424$, $N = 10^5$. (b) The autocorrelation time τ_c obtained from numerical fitting and the theoretical equation $\tau_c = 2r_s^2N/\epsilon^2$, $\alpha = -0.01424$.

with amplitude r_s. The ACF $C_\theta(\tau)$ is a typical damped oscillation with frequency $\omega_1 = \omega_0 + C_i r_s^2$ and correlation time

$$\tau_c = 2r_s^2N/\epsilon^2 \tag{7}$$

To a first-order approximation, we can simply multiply $C_\theta(\tau)$ by r_s^2 to get the correlation function $C(\tau)$ of the state variable $y_1 \approx r\cos\theta$. The corresponding power spectrum density (PSD) of y_1 can then be calculated as the following:

$$PSD(\omega) = 2\int_0^\infty C(\tau)e^{-i\omega\tau}\,d\tau \approx \frac{r_s^2\tau_c}{1 + (\omega - \omega_1)^2\tau_c^2} \tag{8}$$

Clearly, the PSD has a peak at $\omega = \omega_1$, whose height H and half-height width $\Delta\omega$ are $H = r_s^2\tau_c$, $\Delta\omega = 1/\tau_c$ respectively. The SNR, defined as the peak height divided by the half width,[32] reads

$$\mathrm{SNR} = H/\Delta\omega = (r_s\tau_c)^2 = 4r_s^6N^2/\epsilon^4 \tag{9}$$

It can be checked that r_s (τ_c) increases (decreases) monotonically when the system size N is reduced, that is, the oscillation becomes stronger and more irregular. One may expect that for some optimal system size N, the "tradeoff" between the strength and regularity of the NIO gives a maximal SNR, and indicates the occurrence of "system size resonance", also known as "internal noise coherent resonance" (INCR). One should note that INCR here does not correspond to maximum "temporal coherence" of the NIO, that is, the correlation time τ_c shows no maximum. The maximum in SNR just reflects a NIO with intermediate amplitude and temporal coherence, as also pointed out by Ushakov et al.[38]

By $\partial(\mathrm{SNR})/\partial N = 0$, the optimal size reads

$$N_{\mathrm{opt}} = \frac{-C_r\epsilon^2}{4\alpha^2} \tag{10}$$

Equations 6−10 give the main analytical results.

4. Comparison with Simulation

To check the validity of the above analysis, we have performed numerical simulations of eq 1 with a time step 0.001. Time series $u(t)$, $v(t)$, and $w(t)$ were used to calculate $r(t)$ and $\theta(t)$ via eqs 5a and 5b, and $r(t) = \sqrt{y_1^2(t) + y_2^2(t)}$, $\cos\theta(t) = y_1(t)/r(t)$. Probability distribution of $r(t)$ is calculated over a long

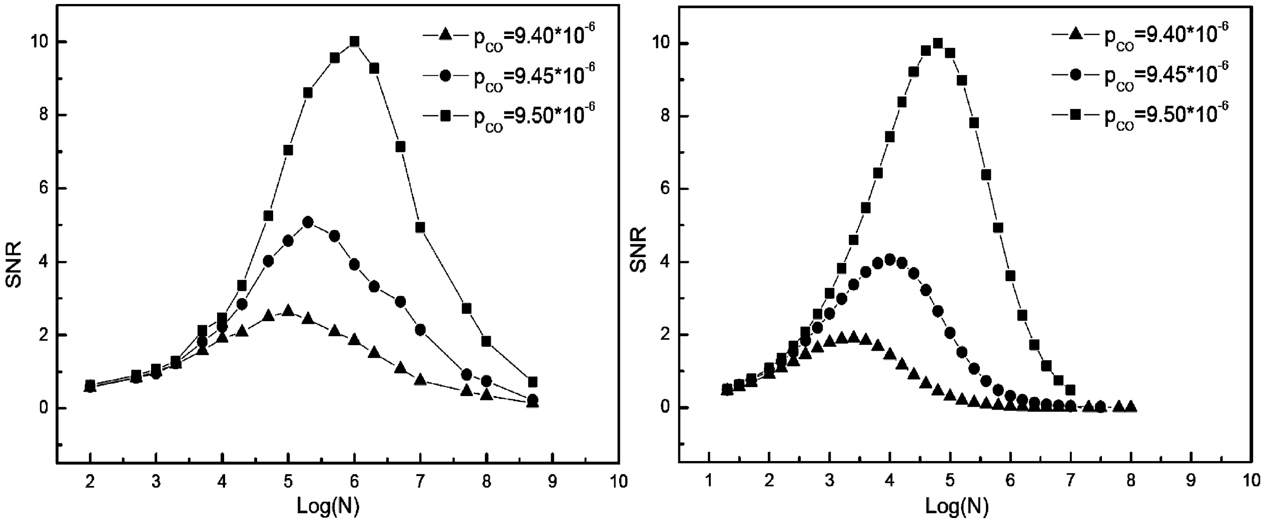

Figure 4. Dependence of the effective SNR on the system size *N* from (a) numerical calculations and (b) analytical results (eq 9).

enough time period. In Figure 2a, the comparison of the stationary distribution of $r(t)$ between the theory and numerical simulation for $p_{CO} = 9.5 \times 10^{-6}$ mbar ($\alpha = -0.00056$) is shown. Excellent agreements are observed. With the increase of N (thus the internal noise level decreases), the distribution becomes wider, and the amplitude of the NIO becomes smaller; see Figure 2b.

The comparison between the ACF of cos $\theta(t)$ obtained from simulation and eq 6b for $p_{CO} = 9.45 \times 10^{-6}$ mbar ($\alpha = -0.01424$) is shown in Figure 3a, and they also show very good agreement. By fitting the peaks in the ACF, one can numerically obtain the correlation time τ_c as a function of system size, which is shown in Figure 3b. Again, the numerical results for $\theta(t)$ show good agreement with the analytical results.

It is known that one often use the correlation time to measure the coherence of oscillation. A longer correlation time often means more temporal “regularity”. But in this system, the NIO does not show a maximal regularity at an intermediate noise level. As shown in Figures 2 and 3, on decreasing the system size N (thus the internal noise level increases) the amplitude of the NIO becomes larger and the correlation time smaller. It is to say that the large noise makes the NIO irregular but strong and small noise makes it regular but weak. The tradeoff between these two leads to the maximum of the SNR, according to eq 9. We depict the dependence of SNR on N in Figure 4, panel a (simulation) and panel b (theory), where good qualitative agreements are apparent; INCR appears, and the optimal size N_{opt} and the maximal SNR both become larger when the distance from the HB decreases. Because correct numerical estimation of the PSD and henceforth SNR of the noisy data is difficult, there are still discrepancies in regard to the exact location of the optimal system size N_{opt} and the maximal value of SNR (note that the absolute values of the SNR do not make sense because the SNR are in arbitrary units). However, the main features observed in the numerical experiments have been well reproduced by the theory.

5. Discussions and Conclusions

Rate oscillations have been observed in many surface reaction systems. Different waveforms of oscillations may be relevant to different reaction activity, selectivity, and rate. Understanding the mechanism of oscillations and how it is affected by environmental or internal noises is thus of both practical and theoretical importance. Due to the growing interest in catalytic reactions in nanosystems,[39] the study of the effect of internal noise is thus an intriguing topic. Although experiments and simulations can provide “first-handed” information, theoretical works are also important, which can help to better understand current experimental observation, and in addition have the ability of prediction, which may help the design of new catalysts.[40] The present work is moving forward toward this direction.

In a recent paper, theoretical analysis was performed to study the effect of internal noise on the bistability behavior in a CO oxidation system.[40] In our present work, we focus on NIO and coherent resonance phenomenon. Equations 6−10 give clear expressions for the quantities of interest, from which one can figure out when and how the internal noise matters without time-consuming simulations. For instance, eq 7 gives the relationship of the correlation time with the system size N and the reaction details (via ϵ^2). And from the expression of $\epsilon^2 = \sum_\rho({\nu_{1\rho}}^2 + {\nu_{2\rho}}^2)\, a_\rho^{(00)}/2$, an important factor besides the system size N that enters the formula of r_s, τ_c, and SNR, we know that different reactions have different “weights” $({\nu_{1\rho}}^2 + {\nu_{2\rho}}^2)\, a_\rho^{(00)}/2$, associated with its reaction rate a_ρ and stoichiometric coefficients $(\nu)_{i\rho}$. Hence, we can figure out how each reaction contributes to the effect of internal noise and how one might control them.

Although the analysis in the present work sheds some new light into the effects of internal fluctuations in surface catalytic reactions, its application is limited by the validity of the CLE (eq 1). Strictly speaking, the CLE is valid only when the surface area considered is well mixed, such that the reaction inside the region is homogeneous. For CO oxidation on an extended single-crystal catalytic surface, such a well-mixed area is determined by the diffusion length of CO on the surface. At low pressures where diffusion of CO on the surface is fast, the well-mixed approximation is good and CLE does work. At high pressures, however, the diffusion length is small and one may need to further consider “diffusion-coupled” subdomains, inside which the reactions are well-mixed, but concentration gradients exist between neighboring subdomains. Very recently, Pineda et al. have introduced a reaction−diffusion master equation to study the fluctuation-induced phase transition for CO oxidation system at high pressures.[41] A similar master equation approach, considering adsorption, diffusion and reaction as stochastic birth−death processes, was also used to show that oscillations can be generated by stochastic ignitions of fronts and pulses in excitable or bistable regions.[42] Our current analysis only applies to a single domain, and it is interesting to take diffusion into account to further investigate the role of internal fluctuations during the formation of spatiotemporal structures in the oscillatory region. Please note that there are other situations under which the current analysis is applicable, for instance, for reactions at low pressure on small areas such as the surface of a nanoparticle or a Pt field emitter tip.

In conclusion, using a mesoscopic stochastic model for CO oxidation on the platinum surface system, the effect of internal noise for this mesoscopic chemical oscillator is studied analytically in the parameter region outside but close to the supercritical HB. By normal form calculation and stochastic averaging procedure, we have analytically studied the NIO and INCR phenomenon. Our theoretical analysis reproduces the numerical results very well. Because internal noises are inevitable in a real system and the occurrence of NIO and stochastic resonance indicates that internal noise can play some nontrivial, constructive roles in the dynamics of heterogeneous catalysis, the present work may also help narrow the gap between experiments and theoretical study of surface catalytic reactions. We hope our analysis could find some interesting application for catalytic reaction and can also open more perspectives in the study of internal noise in nanoscale catalytic systems.

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