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Coherent Resonance for Rate Oscillations During CO Oxidation on Pt(110) Surfaces: Interplay Between Internal and External Noise

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Effects of noise on rate oscillations during CO oxidation on Pt(110) surface were investigated, both theoretically and numerically, by focusing on the interplay of internal noise (IN) due to stochasticity in reaction events, and external noise (EN) resulting from parameter perturbation. The surface is divided into cells of variable size which are assumed to be well mixed, and we consider the behavior inside a single cell. Attention is paid to parameter regions subthreshold of the deterministic Hopf bifurcation, where noise can induce stochastic oscillations, the signal-to-noise ratio (SNR) of which shows a maximum with the variation of noise intensity, known as coherent resonance (CR). By stochastic normal theory, we show that IN and EN contribute in a weighted additive way to an effective noise that lead to CR, such that SNR shows a ridge shape in the D-$1/\sqrt{N}$ plane, where D and $1/\sqrt{N}$ measures the strength of EN and IN, respectively. It is shown that for too large IN (EN), CR behavior with EN (IN) no longer exists. Numerical simulations show good agreements with the theoretical results.

Key words: Fluctuation, Oscillation, Coherent resonance, Surface catalysis

I. INTRODUCTION

Catalytic oxidation of carbon monoxide has attracted much attention for more than two decades, due not only to its application, but also to its complex dynamic behavior of the reaction on nanometer-sized metal particles of supported catalysts [1]. A variety of "dissipative structures" have been observed in heterogeneous catalytic reactions, including multistability, oscillation, chaos, wave, turbulence, and pattern formation [2,3]. At low pressures and typical temperatures, diffusion length is relatively large, the surface can be regarded as being locally well-maxed by the diffusion, and simple mean-field models in the form of deterministic reaction-diffusion equations have been doing well to produce many experimental observations. However, when looking at very small length scales, e.g., when studying the reactions on a field emitter tip [4-6] or the surface of a nanoparticle, internal fluctuations resulting from stochastic reaction and diffusion events become crucial and must be considered. In addition, when the pressure becomes high, the diffusion length may decrease to a scale on which internal fluctuations become crucial. In all these cases, stochastic models should be used instead of deterministic reaction-diffusion ones to describe the system's dynamics. The effect of internal noise has become an important topic in such mesoscopic surface reaction systems.

Recently, growing attention had been paid to the effect of these fluctuations on the kinetics of catalytic CO oxidation. Experimentally, Johánek and co-workers showed that coverage fluctuations on catalyst particles can drastically alter their macroscopic catalytic behavior [7]. It was found that fluctuation can drive transitions between the active and the inactive branch of the reaction for catalytic CO oxidation on a Pt field emitter tip [4-6]. Depending on the noise strength and the fraction of CO, one observes in the deterministically bistable region a large variety of different types of behavior, including island nucleation and growth as well as noise-induced switching. Using stochastic models [8-10], Peskov and co-workers demonstrated that the large difference between the oscillations observed on a 4-nm and 10-nm Pd particles was a consequence of the interplay between the system's nonlinear dynamics and the internal noise. Besides experiments and simulations, analytical methods based on solution of master equations have also been used to study the effect of noise on bistability on Pt surfaces [11-13]. The effects of noise on pattern formation in nanometer scale, known as nonequilibrium nanostructures, have also been deeply studied using mesoscopic models in the form of Langevin equations [14]. To simulate the surface reactions in nanoscale, by accounting for adsorbate-induced surface reconstructing, Zhdanov and coworkers have developed effective Monte Carlo (MC) simulation schemes, in a microscopic manner, to successfully reproduce the bistability, kinetic oscillations, even pattern formation observed in experiments [15-20].

In the present work, we mainly study the effect of noise on CO oxidation on Pt(110) surfaces. Besides

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TABLE I Reaction channels involved in the CO oxidation model.

Reaction step	Transition rate	Description
$N_{CO}\rightarrow N_{CO}+1$	$a_1=P_{CO}k_{CO}s_{CO}(1-u)$	CO adsorption
$N_O\rightarrow N_O+2$	$a_2=1/2\ P_{O_2}\ k_O s_{CO}\ [s_O^{1\times 2}(1-w)+s_O^{1\times 1}w](1-u)^2(1-v)^2$	O_2 adsorption
$N_{CO}\rightarrow N_{CO}-1$	$a_3=[k_{des}^{1\times 2}(1-w)+k_{des}^{1\times 1}w]u$	CO desorption
$N_{CO}\rightarrow N_{CO}-1$, $N_O\rightarrow N_O-1$	$a_4=k_{re}uv$	Reaction
$N_{1\times 1}\rightarrow N_{1\times 1}+1$	$a_5=k_{1\times 1}(1-w)\times f_{1\times 1}(u,w)$	(1×2) to (1×1)
	$f_{1\times 1}(u,w)=(1-\varepsilon)u^\lambda+\varepsilon w^\lambda$	
$N_{1\times 1}\rightarrow N_{1\times 1}-1$	$a_6=k_{1\times 2}w\times f_{1\times 2}(u,w)$,	(1 × 1) to (1×2)
	$f_{1\times 2}(u,w)=(1-\varepsilon)(1-u)^\lambda+\varepsilon(1-w)^\lambda$	

'internal noise (IN)' as stated above, we also take into account 'external noise (EN)', which is also inevitable in real systems. The main question we want to address is the interplay between IN and EN. To this end, we use a mesoscopic model which was proposed in Ref.[12]. The model considers a field emitter tip or a surface area under high pressure such that diffusion length is small. The surface is divided into cells of variable size which are assumed to be well-mixed by diffusion, and the reaction events inside each cell and jump between neighboring cells are stochastic. Similar to Ref.[12], we also consider the behavior inside a single cell in the present work. To account for the effects of both EN and IN, we use the chemical Langevin equation (CLE) as an approximation of the master equation. Note that although the validity of CLE is still under debate, CLE has been used successfully to study qualitatively the effect of internal noise in not too small chemical systems [21-24]. For the purpose of the present work, CLE is a convenient method, because its deterministic part gives one the bifurcation features in the macroscopic limit. This character also makes it possible to use stochastic bifurcation theory to study the effects of noise.

Specifically, we have studied the coherent resonance (CR) phenomenon in the present work. In a parameter region subthreshold to the deterministic oscillatory dynamics, noise (external or internal) can induce oscillation, the performance of which, characterized by a well-defined signal-to-noise ratio (SNR), undergoes a maximum with the variation of noise intensity. Note that noise induced oscillation (NIO) and CR was not new [25-27]; however, the major issue here is the interplay between IN and EN. Only a few recent works addressed this question in other systems. For instance, Hanggi *et al.* have studied CR behavior of a small cluster of ion channels on neuron membrane patches [28], and Gong *et al.* have studied the CR behavior for CO oxidation on the surface of nanoparticles [29]. Note however, these studies were all based on numerical simulations and theoretical analysis is necessary to get a systematic understanding. To this end, we have applied the 'stochastic normal form' theory developed in our recent work [30] that addressed internal noise CR in the Brusselator and extend it to include both EN and IN. It is shown that IN and EN contribute in a 'weighted-additive' way to a well-defined effective noise that lead to CR. One can figure out which one of EN and IN is more important from the weight factors. As predicted by the theory, SNR does show a ridge shape in the D-$1/\sqrt{N}$ parameter plane, where D and $1/\sqrt{N}$ measures the strength of EN and IN, respectively. It is then straightforward to conclude that CR will only exist for small enough IN or EN, and the analytical results are well reproduced by numerical simulations. In this work, we describe the model system, perform the theoretical analysis, and get simulation results.

II. MODEL DESCRIPTION

The system we considered in the present work is CO catalytic oxidation on low-index Pt(110) single crystal surfaces [12], which has been studied extensively by experiment and theory. The catalytic oxidation of CO follows the Langmuir-Hinshelwood mechanism, i.e., CO and O_2 molecules must be adsorbed on the surface before reactions between them take place. Based on the work of Ertl's group, the adsorption-induced surface reconstruction between 1×2 and 1×1 phases must be considered to account for the rate oscillations. Accordingly, there are mainly six reaction steps regarding the change of the system state, which is represented by the number of adsorbed CO molecules N_{CO}, of adsorbed O_2 molecules N_O, and of 1×1 phase $N_{1\times 1}$, as listed in Table I. Therein, P_{CO} and P_{O_2} are partial pressures of CO and O_2; the k_is (with i='re', '1×1', '1×2', 'des') stand for corresponding reaction constants for reaction, phase transitions, desorption, respectively; k_{CO} and k_O are the impingement rates of CO and O_2 to the surface, with sticking coefficients to be s_{CO} and s_O, respectively. Note that the sticking coefficient of O_2 on 1×1 phase is larger than that on 1×2 phase, which is essential to provide a negative-feedback mechanism for the oscillation to happen. All the parameter values are the same as those of Ref.[12], unless given explicitly by other values.

Due to the presence of IN, all these reactions steps are stochastic, allowing the description of the system's

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dynamics by stochastic theories [31]. As stated in the introduction, we consider a well-mixed cell with a total of N adsorption sites, inside which the above steps occur stochastically. According to Gillespie, one can describe the evolution of the system's state by chemical Langevin equations (CLE) [32]:

$$\begin{aligned}\frac{\mathrm{d}u}{\mathrm{d}t} &= (a_1 - a_3 - a_4) + \\ &\quad \frac{1}{\sqrt{N}}\left[\sqrt{a_1}\xi_1(t) - \sqrt{a_3}\xi_3(t) - \sqrt{a_4}\xi_4(t)\right] \\ \frac{\mathrm{d}v}{\mathrm{d}t} &= (2a_2 - a_4) + \frac{1}{\sqrt{N}}\left[2\sqrt{a_2}\xi_2(t) - \sqrt{a_4}\xi_4(t)\right] \\ \frac{\mathrm{d}w}{\mathrm{d}t} &= (a_5 - a_6) + \frac{1}{\sqrt{N}}\left[\sqrt{a_5}\xi_5(t) - \sqrt{a_6}\xi_6(t)\right]\end{aligned} \quad (1)$$

where $u=\frac{N_{\mathrm{CO}}}{N}$, $v=\frac{N_{\mathrm{O}}}{N}$, $w=\frac{N_{1\times1}}{N}$ are concentration-like variables, and $\xi_{i=1,\ldots,6}(t)$ 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 main purpose of the present work is to study the interplay between IN and EN. Generally, EN may result from the fluctuations in the pressure, temperature, etc, that may be coupled to the system's dynamics in additive or multiplicative ways. It is worth noting here that the following analysis in the present work can be extended to more general cases. For simplicity here, we just assume that the partial pressure of CO is subjected to noise, i.e.,

$$P_{\mathrm{CO}} = P^0_{\mathrm{CO}} \times [1 + D\eta(t)] \quad (2)$$

where $\eta(t)$ is a Gaussian white noise with $\langle\eta(t)\rangle=0$ and $\langle\eta(t)\,\eta(t')\rangle=\delta(t-t')$, and D denotes EN-intensity. This additional external noise will add one more term to the right hand side of Eq.(1),

$$\begin{aligned}\frac{\mathrm{d}u}{\mathrm{d}t} &= (a_1 - a_3 - a_4) + D\cdot a_1\eta(t) + \\ &\quad \frac{1}{\sqrt{N}}\left[\sqrt{a_1}\xi_1(t) - \sqrt{a_3}\xi_3(t) - \sqrt{a_4}\xi_4(t)\right]\end{aligned} \quad (3)$$

Strictly speaking, the perturbation to P_{CO} should also change the internal noise terms in the bracket; however, since the external noise is assumed to be independent to the internal noise, and both D and $1/\sqrt{N}$ are considered to be small, this second-order perturbation can be ignored.

If noises are not considered, the deterministic system shows very abundant bifurcation features including Hopf bifurcation (HB), as described in Ref.[12]. In the present work, we mainly focus on the effects of noises in the parameter region outside but close to the HB, where coherent resonance (CR) exists. In the following part, we will extend the analysis in Ref.[30] to the case considered here, where both EN and IN exist.

III. THEORETICAL ANALYSIS

For fixed parameters p_{O_2}=2 mPa and T=520 K, the deterministic system, obtained by removing the noise terms from Eq.(1), has a supercritical HB at $p^{\mathrm{H}}_{\mathrm{CO}}\cong$950.2 μPa. According to the Hopf theorem [33], the Jacobi matrix $(\mathbf{J})_{ij}=\partial F_i(\{x_i\})/\partial x_j$, evaluated at the fixed point $\mathbf{x}_s=(u_s\,v_s\,w_s)'$ (here $'$ stands for vector transpose), has a pair of conjugate eigenvalues $\lambda_\pm=\alpha\pm i\omega_0$ for $p_{\mathrm{CO}}\cong p^{\mathrm{H}}_{\mathrm{CO}}$, with $\alpha<0(>0)$ for $p_{\mathrm{CO}}<p^{\mathrm{H}}_{\mathrm{CO}}(>p^{\mathrm{H}}_{\mathrm{CO}})$. The other eigenvalue λ_3 of $\mathbf{J}$ has strictly negative real parts. In the very near vicinity of the HB, the behavior of the deterministic system can be described by a normal from, governing the dynamics of a complex magnitude Z on the two-dimensional center manifold spanned by the eigenvector of $\lambda_\pm$. For a three variable deterministic system as considered here, $Z=y_1+iy_2$, where the new vector $\mathbf{y}=(y_1\,y_2\,y_3)'$ is linearly transformed from $\mathbf{x}=(u\,v\,w)'$ via $\mathbf{y}=\mathbf{T}^{-1}(\mathbf{x}-\mathbf{x}_s)$. The matrix $\mathbf{T}$ is constructed by $(\mathrm{Re}\mathbf{u}_+\ -\mathrm{Im}\mathbf{u}_+\ \mathbf{u}_3)$, where $\mathbf{u}_+$ (normalized so that its first non-vanishing component is 1) is the eigenvector of $\mathbf{J}$ corresponding to λ_+ and $\mathbf{u_3}$ is the eigenvector of λ_3 [33]. More details of normal form can be found in standard textbooks of bifurcation theory.

When taking into account the types of noise, the same normal form transformation can be performed for deterministic terms. What is new is that the linear transformation of variables will lead to a linear combination of noise terms. One should note here that to perform ordinary variable transformation, the stochastic differential Eq.(1) must be interpreted in a Stratonovich manner. Although we can assume that this is the case for the external noise, the CLE must be interpreted in the Ito manner to be consistent with the master equation. Therefore, to be physically strict, one should first transform the CLE into Stratonovich form. However, as already verified in our previous work [30], this procedure will only lead to a correction of order $1/N$, and can be ignored. Consequently, we can obtain the following 'stochastic normal form' from Eqs.(1) and (3):

$$\begin{aligned}\frac{\mathrm{d}Z}{\mathrm{d}t} &= (\alpha + i\omega_0)Z + (C_r + iC_i)|Z|^2 Z + \\ &\quad \frac{1}{\sqrt{V}}\sum_{\rho=1}^{6}(\tilde{v}_{1\rho} + i\tilde{v}_{2\rho})\sqrt{a_\rho}\circ\xi_\rho(t) + \\ &\quad D\cdot(\tilde{v}_{11} + i\tilde{v}_{21})\,a_1\circ\eta(t)\end{aligned} \quad (4)$$

Here, we have used the notation of stoichiometric coefficient matrix $(\mathbf{v})_{i\rho}$, which gives the change of number of i^{th} molecules through reaction channel ρ. According to the reaction mechanisms listed in Table I, for instance, one has $v_{1\rho=1,\ldots,6}$=(1 0 −1 −1 0 0) for CO molecules. Then the coefficients with tilde in Eq.(4) are obtained by $(\tilde{\mathbf{v}})_{i\rho} = \left(\mathbf{T}^{-1}\mathbf{v}\right)_{i\rho}$. C_r and C_i are constants determined by the nonlinear terms in the equation; they can be calculated numerically, and the result is C_r=−5.27897, C_i=3.86874 at the HB. '$\circ$' stands

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for Stratonovich interpretation of the noise. Writing $Z = re^{i\theta}$, we have:

$$\begin{aligned}
\frac{\mathrm{d}r}{\mathrm{d}t} &= \left(\alpha r + C_r r^3\right) + D\chi_{rD} \circ \eta\left(t\right) + \\
&\quad \frac{1}{\sqrt{N}} \sum \rho\chi_{r\rho} \circ \xi_\rho\left(t\right) \\
\frac{\mathrm{d}\theta}{\mathrm{d}t} &= \left(\omega_0 + C_i r^2\right) + D\chi_{\theta D} \circ \eta\left(t\right) + \\
&\quad \frac{1}{\sqrt{N}} \sum \rho\chi_{\theta\rho} \circ \xi_\rho\left(t\right) \qquad (5) \\
\chi_{r\rho} &= \left(\tilde{\nu}_{1\rho}\cos\theta + \tilde{\nu}_{2\rho}\sin\theta\right)\sqrt{a_\rho} \\
\chi_{\theta\rho} &= \left(-\tilde{\nu}_{1\rho}\sin\theta + \tilde{\nu}_{2\rho}\cos\theta\right)\sqrt{a_\rho}/r \\
\chi_{rD} &= \left(\tilde{\nu}_{11}\cos\theta + \tilde{\nu}_{21}\sin\theta\right)a_1 \\
\chi_{\theta D} &= \left(-\tilde{\nu}_{11}\sin\theta + \tilde{\nu}_{21}\cos\theta\right)a_1/r
\end{aligned}$$

Clearly, r and θ are strongly coupled to each other in Eq.(5), rendering the direct solution of it a difficult task. Notice the facts that $|\alpha| \ll 1$ near the HB and both D and $1/\sqrt{N}$ are considered to be small allow us to use the 'stochastic averaging' method which approximate the system as Markov processes in the long time limit [33]. Keeping to the lowest order, we can finally reach the following stochastic normal form in a quite simple form:

$$\begin{aligned}
\frac{\mathrm{d}r}{\mathrm{d}t} &= \left(\alpha r + C_r r^3 + \frac{\sigma^2}{2r}\right) + \sigma\xi_r\left(t\right) \\
\frac{\mathrm{d}\theta}{\mathrm{d}t} &= \left(\omega_0 + C_i r^2\right) + \frac{\sigma}{r}\xi_\theta\left(t\right) \qquad (6)
\end{aligned}$$

where ξ_r and ξ_θ are two new independent Gaussian white noises with zero mean and unit variance. σ is the effective noise strength, which has the explicit form:

$$\begin{aligned}
\sigma^2 &= \frac{\sum_{\rho=1}^{6}\left(\tilde{v}_{1\rho}^2 + \tilde{v}_{2\rho}^2\right)a_\rho^{(00)}}{2}\left(\frac{1}{\sqrt{N}}\right)^2 + \\
&\quad \frac{(\tilde{v}_{11}^2 + \tilde{v}_{21}^2)[a_1^{(00)}]^2}{2}D^2 \qquad (7) \\
a_\rho &= \sum_{k+l=0}^{n} a_\rho^{(kl)}\left(r\cos\theta\right)^k\left(r\sin\theta\right)^l
\end{aligned}$$

where $a_\rho^{(00)}$ is the coefficient with k=l=0 in the expansion of reaction rates a_ρ.

Eq.(6) is in the same form as Eq.(5) in Ref.[30], and the remaining analysis is similar. The key point is that r and θ are now separated in Eq.(6), such that analytic solution is available. From Eq. (6), the stationary distribution of r reads,

$$p_s\left(r\right) = C_0 r\exp\left(\frac{2\alpha r^2 + C_r r^4}{2\sigma^2}\right) \qquad (8)$$

where C_0 is the normalization constant. By $\dfrac{\partial p_s\left(r\right)}{\partial r}$=0, one gets the most probable radius r_s of the NIO,

$$r_s = \left(\frac{\sqrt{\alpha^2 - 2C_r\sigma^2} + \alpha}{-2C_r}\right)^{1/2} \qquad (9)$$

Then from Eq.(6), we can obtain the correlation function of y_1=$r\cos\theta$, to keep the leading term,

$$\begin{aligned}
C\left(\tau\right) &= \lim_{t\to\infty}\langle r\cos\left[\theta(t)\right] r\cos\left[\theta(t+\tau)\right]\rangle \\
&\cong \frac{1}{2}{r_s}^2\cos(\omega_1\tau)\exp\left(-\frac{\tau}{\tau_c}\right) \qquad (10)
\end{aligned}$$

where $\omega_1 \simeq \omega_0 + C_i {r_s}^2$ and the correlation time τ_c reads,

$$\tau_\mathrm{c} = \frac{2{r_s}^2}{\sigma^2} \qquad (11)$$

Fourier transformation of $C(\tau)$ gives the power spectrum density (PSD), $\mathrm{PSD}(\omega)$=$\dfrac{{r_s}^2\tau_c}{1 + \left(\omega - \omega_1\right)^2{\tau_c}^2}$, which has a clear peak at ω_1. By definition, the SNR of the NIO is the height of the peak divided by the half-height width,

$$\mathrm{SNR} = \left(r_s\tau_c\right)^2 = \frac{4{r_s}^6}{\sigma^4} \qquad (12)$$

It is easy to check that τ_c decreases and r_s increases, both monotonically, when the effective noise intensity σ increases. Therefore, one expects that $r_s \times \tau_\mathrm{c}$ may show a maximum with the variation of σ, which corresponds to the occurrence of CR. By $\dfrac{\partial\left(\mathrm{SNR}\right)}{\partial\left(\sigma^2\right)}$=0, the optimal noise intensity for coherent resonance satisfies:

$${\sigma_\mathrm{opt}}^2 = \frac{4\alpha^2}{-C_r} \qquad (13)$$

Eq.(8) to Eq.(13) can be compared to numerical experiments.

From above analysis, especially Eq.(7), we can conclude that IN and EN contribute in a 'weighted additive' manner to the effective noise intensity σ^2. For a given reaction channel ρ, the weight is proportional to $(\tilde{v}_{1\rho}^2$+$\tilde{v}_{2\rho}^2)a_\rho^{(00)}$, which depends on the details of that reaction such as the reaction rate and stoichiometric coefficients. Since EN is added to P_CO, which is involved in a_1, we can see that the weight factor of EN also depends on a_1. The main consequence of this weighted additive feature can be outlined.

(i) According to Eqs.(7) and (13), in the parameter space of D-$1/\sqrt{N}$, SNR will show a 'ridge' shape, with the ridge line to be part of an ellipse

$$pD^2 + q\left(\frac{1}{\sqrt{N}}\right)^2 = \frac{4\alpha^2}{-C_r} \qquad (14)$$

where p, q are coefficients given by Eq.(7). For the parameters chosen in the present work, we have p=1.7202 and q=1.5709.

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(ii) For a fixed $D<D_c=\sqrt{4\alpha^2/(-C_r p)}$, Eq.(14) may have solution for N, where the SNR shows maximum. This corresponds to 'internal noise coherent resonance (IN-CR)' reported in a variety of literature [21-25,34-37], while for $D>D_c$, no IN-CR would happen.

(iii) Similarly for a fixed system size $N>N_c=\dfrac{-C_r q}{4\alpha^2}$, i.e., the internal noise is weak, CR with EN could happen at some optimal D. If the system size is too small, one would not expect EN-CR to happen. Actually, such a behavior has been reported by Hänggi *et al.* [28], where the authors stated that CR with EN was a collective behavior of ion-channels.

IV. SIMULATION RESULTS

To demonstrate the validity of above theoretical analysis, we have numerically simulated Eq.(1) and Eq.(3) by Eular methods with a time step of 0.001. After a long transient time, $r(t)$ is calculated as $r(t)=\sqrt{y_1{}^2(t)+y_2{}^2(t)}$, where the vector $\mathbf{y}=(y_1\ y_2\ y_3)'$ is calculated via $\mathbf{y}=\mathbf{T}^{-1}(\mathbf{x}-\mathbf{x}_s)$. Accordingly, we have $\cos\theta(t)=y_1(t)/r(t)$. Probability distribution of $r(t)$ is calculated over a long enough time period. In Fig.1, the comparison of the stationary distribution of between the theory and numerical simulation, for p^0_{CO}=950 μPa ($\alpha=-556.5\times10^{-6}$), is shown. Excellent agreements are observed, especially for small noise levels. In Fig.1(a), external noise intensity D is fixed to be 10^{-4} which is small enough. With the increment of internal noise level (N decrease), the distribution becomes wider, and the most probable value of $r(t)$ becomes larger. Similar results are shown in Fig.1(b) in which we fix N to be 10^8 and change D from $10^{-2.5}$ to $10^{-3.5}$.

The autocorrelation function (ACF) of $\cos\theta(t)$ obtained from simulation and Eq.(10) are shown in Fig.2 (a) and (c), for p_{CO}=945 μPa ($\alpha=-14.23\times10^{-3}$). By fitting the peaks in the ACF, one can numerically obtain the correlation time as a function of the noise intensity, which is shown in Fig.2 (b) and (c), where the solid lines are drawn from the theoretical result Eq.(11). Good agreement between simulation and theory are also observed.

According to the definition of SNR in this work, three typical curves of SNR as a function of lg$D$ for different IN intensity are described in Fig.3. It can be seen that when system size $N=10^9>N_c=10^{6.826}$, the SNR can clearly show maximum $D\approx10^{-3.4}$. Interestingly, when $N=10^{6.5}$ is slightly smaller than N_c, the peak disappears and there exists a plateau in this case. With further reduction of N , for example, $N=10^4$, the SNR is very low no matter how strong the EN is, i.e., no CR happen. Symbols are obtained from simulation data and lines are theoretical results. Quite similar features are observed when one fix D and draw SNR as a function of $\lg(1/\sqrt{N})$ (not shown). To get a global view, we depict the contour plot of SNR in the D-$1/\sqrt{N}$ parameter plane in Fig.4, obtained from Eq.(12). Since Figs.1, 2, and 3 already demonstrate the validity of the theory, we have not shown the SNR contour plot obtained from numerical simulation here. The three points drawn in the last section can be clearly observed.

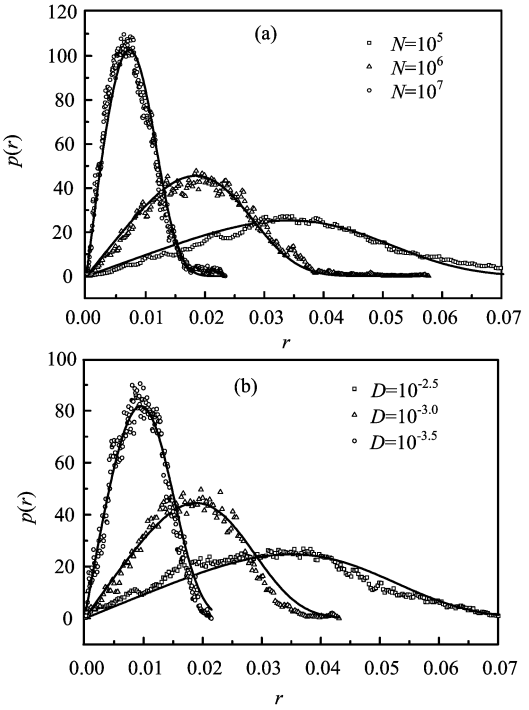

FIG. 1 Stationary distribution of the radius of the noise-induced limit cycle obtained from simulation (symbols) and Eq.(8) (solid line) with $\alpha=-556.5\times10^{-6}$. (a) $D=10^{-4}$ and (b) $N=10^8$.

V. CONCLUSION AND DISCUSSION

In real catalytic reactions systems, IN and EN always coexist. The question is then which one is more important and how they interact with each other. Based on the analysis in the present work, in a parameter region subthreshold to deterministic Hopf bifurcation, IN and EN act in a cooperative way to induce the oscillation. The relative importance of IN is determined by the weight factor q in Eq.(14), where all the reaction channels are relevant. On the other hand, the weight of EN depends on how it is coupled to the system. For the case considered here, EN is assumed to perturb the partial pressure of CO only, which contributes an additional term to a_1, such that the weight p is related to $a_1{}^{(00)}$. For other cases, for instance, if EN is additive to Eq.(1), or p_{O_2} is subjected to parametric noise, the EN term in Eq.(3) and henceforth the expression of p will be different. Although for each case, one needs to recalculate p, the analyses are similar and straightforward following the procedure from Eq.(4) to Eq.(14). It is also possible to extend the analysis to quite general cases

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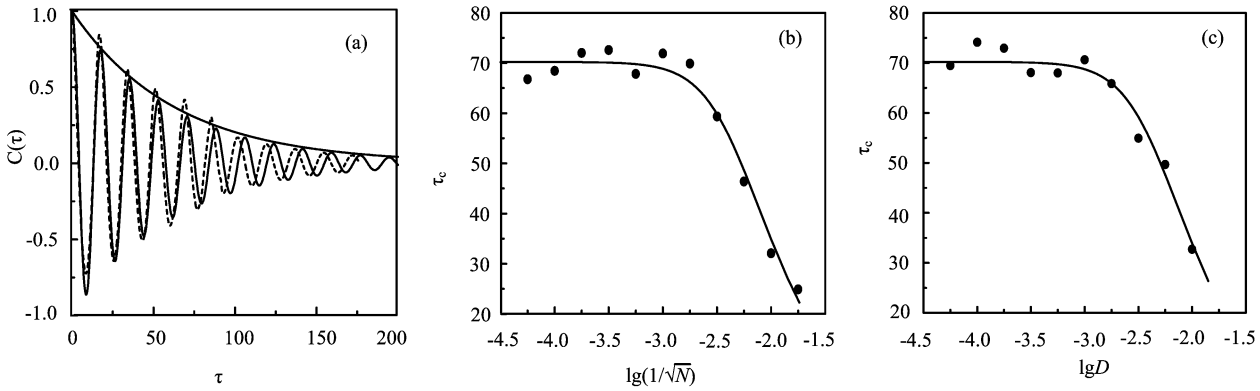

FIG. 2 (a) A typical autocorrelation function obtained from the theoretical formula, Eq.(10) (solid line) and numerical calculations (dashed line). From the exponential fitting we can calculate approximately the autocorrelation time. Parameters are α=-14.23×10^{-3}. D=10^{-4}, $\sqrt{N}$=$10^{2.5}$. The autocorrelation time τ_c obtained from numerical fitting and the theoretical formula $\tau_c = 2{r_s}^2/\varepsilon^2$ for α=-14.23×10^{-3} is shown in (b) external noise D=10^{-4}, and (c) internal noise $\sqrt{N}$=10^4.

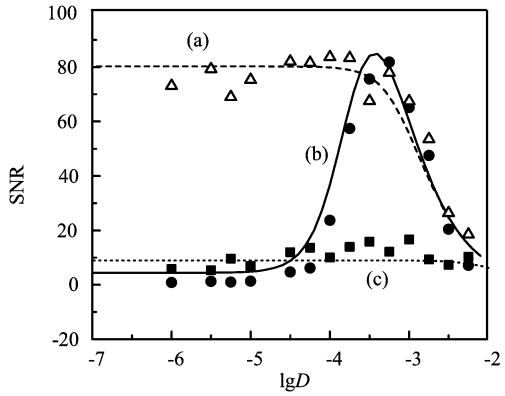

FIG. 3 Dependence of the effective SNR on EN intensity (lg$D$) for different system size N from analytical results (Eq.(12)) (lines) and numerical calculations (symbols). (a) N=$10^{6.5}$, (b) N=10^9, and (c) N=10^4.

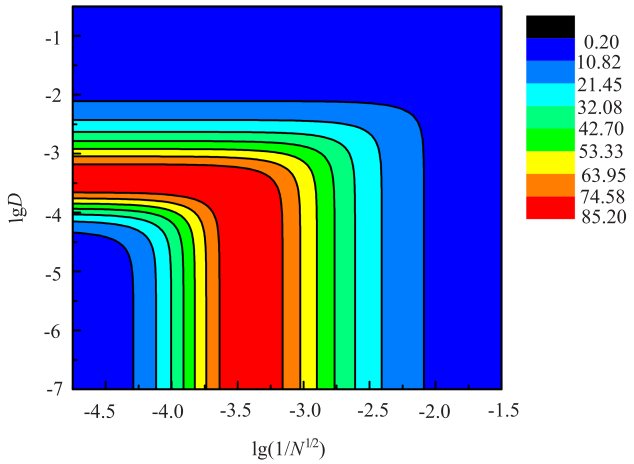

FIG. 4 Contour plot of the effective SNR in the parameter plane of D~$1/\sqrt{N}$ according to Eq. (12).

where EN may come from multiple sources, coupled to the system additively or multiplicatively. By evaluating the 'weight' factor of each source, one can figure out which EN source is more crucial to the system's dynamics. For the parameters chosen in the present study, we see that the weights of EN and IN are nearly the same, so both EN and IN must be considered in a nearly equal way. Based on the analysis here, the system shows CR behavior near the Hopf bifurcation with an "effective noise", rather than EN or IN alone. Constructive roles of EN, i.e., EN-CR, can only be observed when IN is small (N is large), giving EN-CR a collective behavior [27]. Similarly, IN-CR, which is also known as system size resonance [21-25,30,34-37], only exists when EN is small. Though one may obtain these results by numerical simulations, theoretical analysis here provides a clear picture.

Effects of fluctuations on chemical oscillation in small systems were also investigated, by direct MC methods or master equation analysis [15-20,38-41]. Using MC method, Zhdanov's group has studied a lot of kinetic oscillation behaviors in heterogeneous catalytic reaction systems. They used lattice-gas models to mimic the surface reaction, and considered the surface reconstruction from atomic detail. Specifically, they have also considered the effect of lattice size on the oscillation, and found 'reasonable' oscillations even down to 15×15 lattice [39]. On the other hand, Gaspard has studied the correlation time of mesoscopic chemical oscillation using Hamiltom-Jacobi description of the master equation, and got the conclusion that for system size less than a critical value, no 'reasonable' oscillation exists [40,41]. Compared to these results, this work mainly focuses on the region close to the deterministic Hopf bifurcation point where CR exists.

In conclusion, we have studied the effect of IN and EN for rate oscillation during CO oxidation on small surface area, mainly theoretically and verified by numerical simulations. The theoretical analysis is based on the

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stochastic normal form theory proposed in our recent paper [30]. We show that IN and EN contributed in a weighted additive way to an effective noise that leads to CR, and the weight factors depend on the reaction details and how the EN is coupled to the system. The analysis sheds some new light on the important roles of noise in mesoscopic chemical oscillation systems, and may also open perspectives in future theoretical or experimental studies.

VI. ACKNOWLEDGMENT

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