# Internal Noise Stochastic Resonance in NO Reduction by CO on Platinum Surfaces

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We have studied the roles of internal noise in the oscillatory reaction kinetics during NO reduction by CO on low-index single crystal platinum surfaces using the chemical Langevin equation and the Poisson approximation algorithm. Considering that the surface is divided into small well-mixed cells, we have focused on the dynamical behavior inside a single cell. It is found that internal noise can induce rate oscillations and the performance of the stochastic rate oscillations undergoes a maximum with the variation of internal noise level for a given NO partial pressure, demonstrating the occurrence of internal noise stochastic resonance. Such a phenomenon is robust to the change of external parameters, such as NO pressures. Interestingly, it is also found that internal noise noticeably alters the oscillatory waveform and, hence, the reaction activity and oscillation signal intensity, but it nearly does not change the global reaction rate.

## 1. Introduction

In the past several decades, the kinetics of heterogeneous surface catalytic reactions has been extensively studied due to rich nonlinear phenomena involved in the reactions, and much attention has been paid to the influence of heterogeneity and environmental fluctuations of temperature and pressure on the kinetics. However, reactant molecule fluctuation is another important ingredient for small scale reaction systems, and it is generally accepted that the strength of internal noise is inversely proportional to the square root of the system size. Recently, the effects of internal noise in catalytic reaction over single crystal surfaces and nanometer-sized catalyst particles have received growing research interests.[1−12] It was found that internal noise can induce transitions between the active and inactive branch of the reaction for catalytic CO oxidation on a Pt field emitter tip[1,2] and becomes essential in the dynamic behavior of catalytic CO oxidation when surface cells over low-index single crystal surfaces are very small.[3] In the study of spatiotemporal self-organization in the catalytic oxidation of hydrogen on Pt(111), it is suggested that a mesoscopic stochastic model involving internal noise should be used to quantitatively explain the experimental observations.[4] It was demonstrated that the large difference between the reaction dynamical behavior observed on 4-nm and 10-nm palladium particles was a consequence of the interplay between the system's nonlinear dynamics and the internal noise.[5−7] Monte Carlo (MC) simulations of surface catalytic reactions on a small scale surface of a single crystal and of nanometer-sized catalyst particles have shown that the role of fluctuations increases with decreasing size, *L*, and accordingly, there is no guarantee that the mean-field (MF) theory can apply to such systems.[8−11] Very recently, experimental study has shown that coverage fluctuations on catalytic particles can drastically alter their macroscopic catalytic behavior, causing bistabilities to vanish completely with decreasing particle size.[12] All these works provide clear information that internal noise would significantly influence the oscillatory kinetics of catalytic reactions in small scale systems.

Despite these successes in the understanding of the dependence of catalytic reaction kinetics on the internal noise, there is another important type of positive effect of internal noise like that of stochastic resonance (SR) in many physical and biological systems.[13,14] Jung and Hänggi's group demonstrated that optimal internal noise of ion channel clusters can enhance the encoding of a subthreshold stimulus via the *system size resonance*[15,16] and influence the synchronization between the spiking activity of the excitable membrane and an externally applied periodic signal.[17] They have recently shown that channel block (poisoning) may execute significant influence on spiking activity and the regularity of the spike train.[18,19] They also demonstrated that optimal intracellular calcium signaling appears at a certain size or distribution of the ion channel clusters.[20−22] Taking into account the stochastic nature of calcium and fast potassium channel currents in the Plant model of a bursting neuron, noise can induce coherent bursting even in the case when the deterministic neuron is silent.[23]

Our recent studies have shown that internal noise can play constructive SR-like roles in small scale chemical or biochemical reaction systems via internal noise SR, inducing intrinsic stochastic oscillation and optimizing oscillation regularity.[24,25] Very recently, we have found novel SR-like roles of internal noise, that is, the system size biresonance, in intracellular calcium signaling,[26] and the internal noise SR in catalytic CO oxidation on nanometer-sized palladium particles.[27]

In catalytic reactions, most of the studies concerning the internal noise effect have so far focused on the kinetics of catalytic CO oxidation on single crystal or nanometer-sized catalyst particles. Few studies, however, have contributed to the internal noise effect on the NO reduction by CO on Pt single crystals. It is well-known that the NO + CO reaction is one of the most important surface catalytic reactions, in which there are fruitful nonlinear dynamical phenomena involving chemical oscillations, chaos, and spatiotemporal patterns. Therefore, it

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is of importance and significance to investigate the effect of internal noise on the reaction oscillations inside a cell on a Pt(100) surface. Very recently, the MC simulation of NO reduction by CO on small scale single crystal surfaces demonstrated that the oscillations become appreciably and completely irregular when the lattice size decreases down to $L = 20$ and 10, respectively,[28] indicating that fluctuations in this case are becoming large enough and the MF theory would not be applicable for such small scale systems. An important question arises about whether there is an optimal internal noise to favor the oscillations of the reaction.

Here, in the present paper, we have developed a simple stochastic model for the NO + CO reaction and studied the influence of internal noise on the reaction oscillations. We consider that the surface is divided into small cells inside which the reactant molecules are well-mixed, and the reactions inside each cell as well as the exchange of particles between neighboring cells are both stochastic. Therefore, the surface is heterogeneous in a large scale but homogeneous in small scales. Interestingly, we find that internal noise can play rather nontrivial roles. It can induce stochastic oscillations which are distinct from random fluctuations in that there is a clear peak in the power spectrum. An optimal internal noise where the oscillations become the most pronounced does exist, which is characterized by effective SNR which goes through a maximum with the variation of the internal noise level, indicating the occurrence of the *internal noise SR*. Internal noise noticeably alters the oscillatory waveform and hence the reaction activity and oscillation signal intensity, but it nearly does not change the global reaction rate.

## 2. Mesoscopic Stochastic Model

Neglecting the process of $N_2O$ due to its slow formation, the mechanism of NO + CO reaction on Pt(100) following a Langmuir−Hinshelwood scheme can be described by the following sequence of steps:[29,30]

$$\mathrm{CO_{gas}} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{CO_{ads}},\quad \mathrm{NO_{gas}} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \mathrm{NO_{ads}},\quad \mathrm{NO_{ads}} \xrightarrow{k_5} \mathrm{N_{ads}} + \mathrm{O_{ads}},$$
$$2\mathrm{N_{ads}} \rightarrow (\mathrm{N_2})_{gas},\quad \mathrm{CO_{ads}} + \mathrm{O_{ads}} \xrightarrow{k_6} (\mathrm{CO_2})_{gas} \qquad (1)$$

For comparison, it is useful to briefly review the deterministic kinetics of the reaction. In the case of a reaction occurring on extended single crystal surfaces, there are a great number of reacting molecules and, hence, coverage fluctuations are extremely small and can be ignored. The system is described by a simple three-variable system of equations for the variation in the adsorbed CO, NO, and oxygen coverage:[30]

$$\frac{d\theta_{CO}}{dt} = k_1 P_{CO}(1 - \theta_{CO} - \theta_{NO}) - k_2\theta_{CO} - k_6\theta_{CO}\theta_O$$
$$\frac{d\theta_{NO}}{dt} = k_1 P_{NO}(1 - \theta_{CO} - \theta_{NO}) - k_4\theta_{NO} - k_5\theta_{NO}\theta_{empty} \qquad (2)$$
$$\frac{d\theta_O}{dt} = k_5\theta_{NO}\theta_{empty} - k_6\theta_{CO}\theta_O$$

with

$$\theta_{empty} = \max\left[\left(1 - \frac{\theta_{CO} + \theta_{NO}}{\theta^{inh}_{CO,NO}} - \frac{\theta_O}{\theta^{inh}_O}\right), 0\right]$$

**TABLE 1: Constants Used in the Model**[a]

| description | constant | $E_i$ (kcal/mol) | $\nu_i$ |
|---|---|---|---|
| CO/NO adsorption | $k_1/k_3$ | | |
| CO desorption | $k_2$ | 37.5 ($\theta = 0$) | $1.0 \times 10^{14}$ |
| $CO_{ad} + O_{ad}$ reaction | $k_6$ | 14.0 | $2.0 \times 10^8$ |
| NO desorption | $k_4$ | 37.0 ($\theta = 0$) | $1.7 \times 10^{14}$ |
| NO dissociation | $k_5$ | 28.5 | $2.0 \times 10^{15}$ |
| CO/NO repulsion | $k_7$ | 24 | |
| Inhibition coverage for NO dissociation | $\theta^{inh}_{CO,NO}$ | 0.61 | |
| | $\theta^{inh}_O$ | 0.4 | |

[a] The temperature dependence is expressed via an Arrhenius law, $k_i = \nu_i \exp(-E_i/RT)$. Note that all parameters are from refs 29 and 30 and references therein.

where $\theta_{CO,NO,O}$ stand for the adsorbed coverage of CO, NO, and oxygen, respectively. These equations consist of the adsorption and desorption of NO and CO ($k_1$, $k_2$, $k_3$, and $k_4$), the dissociation of NO ($k_5$), and the surface reaction between adsorbed oxygen and adsorbed CO to form $CO_2$ ($k_6$). $P_{CO}$ and $P_{NO}$ are the respective partial pressures of CO and NO gas. The number of vacant sites available for NO dissociation, $\theta_{empty}$, can be calculated from the inhibition coverage, $\theta^{inh}_x$, for NO dissociations of each individual adsorbate. These inhibition coverages could be approximated from experimental observations. The various constants used in the equations are given in Table 1. Two of the constants, $k_2$ and $k_4$, were made coverage dependent, which is crucial for the oscillations in this model. Using experimental values for the system Pt(100)/CO, the coverage dependence of the adsorption energy, $E_{ad}^{CO,NO}$, was parametrized for both gases with the same fitting parameter, $k_7$, by

$$E^{CO,NO}_{ad}(\theta) = E^{CO,NO}_{ad}(0) - k_7\theta^2$$

with $\theta$ denoting the sum of the CO and NO coverages, $\theta = \theta_{NO} + \theta_{CO}$ (see refs 29 and 30 for details).

However, when the reaction takes place on finite or small surfaces, for example, a nanometer-sized particle surface[6,7]or a single cell on a crystal surface,[1,2] fluctuations become crucial due to the existence of very few adsorption sites and stochastic models are required. Furthermore, since the adsorption rates grow proportionally to the partial pressures, while surface diffusion remains unchanged, a description with deterministic equations become less accurate when pressures are increased. The diffusion length may, at higher pressures, decrease until it reaches a scale on which fluctuations become important, so that again stochastic models should be more appropriate. In the following, we will focus our study on the reaction inside one single cell over Pt(100), that is, the spatially homogeneous case.

To take into account the random fluctuations of reactant coverage inside the cell, we have developed a simple stochastic model describing the reaction. Following refs 6 and 7, the variables of the model are the numbers of reacting molecules, $N_{CO}$ and $N_{NO}$, and oxygen atoms, $N_O$, which vary from 0 to $N_S$ (the number of adsorption sites on the cell surface, that is, cell size). The elementary steps (1) are converted into the elementary events and probabilities per unit time $a_i$, which are listed in Table 2.

Usually, one should describe the system's dynamics by a chemical master equation, which depicts the time evolution of the probability of having a given number of $N_{CO}$, $N_{NO}$, and $N_O$. There is not a general procedure for solving this master equation analytically, but it provides the starting point for numerical simulations. Recently, the chemical Langevin equation (CLE)[31] and stochastic simulation algorithm based on the Poisson

**TABLE 2: Stochastic Processes and Transition Rates for NO Reduction by CO inside One Single Cell on Pt(100)**[a]

| stochastic process | reaction rate |
|---|---|
| $N_{CO} \rightarrow N_{CO} + 1$ | $a_1 = k_1 P_{CO}(N_S - N_{CO} - N_{NO})$ |
| $N_{CO} \rightarrow N_{CO} - 1$ | $a_2 = k_2 N_{CO}$ |
| $N_{NO} \rightarrow N_{NO} + 1$ | $a_3 = k_1 P_{NO}(N_S - N_{CO} - N_{NO})$ |
| $N_{NO} \xrightarrow{\text{desorption}} N_{NO} - 1$ | $a_4 = k_4 N_{NO}$ |
| $N_{NO} \xrightarrow{\text{dissociation}} N_{NO} - 1$ | $a_5 = k_5 N_{NO} N_{empty}/N_S$ |
| $\left(\begin{array}{l} N_N \rightarrow N_N + 1,\ N_O \rightarrow N_O + 1, \\ N_{empty} = \max\{[N_S - (N_{CO} + N_{NO})/0.61 - N_O/0.4]N_S, 0\} \end{array}\right)$ | |
| $(N_{CO}, N_O) \rightarrow (N_{CO} - 1, N_O - 1)$ | $a_6 = k_6 N_{CO} N_O/N_S$ |

[a] Note that all parameter values are listed in Table 1.

approximation (PA)[32] were developed. The CLE, a good approximation of the master equation, has been demonstrated as a valid method for the case of having a moderate number of reacting particles in the system.[24−27]

Given the stochastic processes shown in Table 2, the CLE for the current model reads as

$$\begin{aligned} d\theta_{CO}/dt &= \frac{1}{N_S}[(a_1 - a_2 - a_6) + \sqrt{a_1}\xi_1 - \sqrt{a_2}\xi_2 - \sqrt{a_6}\xi_6] \\ d\theta_{NO}/dt &= \frac{1}{N_S}[(a_3 - a_4 - a_5) + \sqrt{a_3}\xi_3 - \sqrt{a_4}\xi_4 - \sqrt{a_5}\xi_5] \\ d\theta_{O}/dt &= \frac{1}{N_S}[(a_5 - a_6) + \sqrt{a_5}\xi_5 - \sqrt{a_6}\xi_6] \end{aligned} \quad (3)$$

where $\xi_i(t)$ ($i = 1, ..., 6$) are Gaussian white noises with $\langle \xi_i(t) \rangle = 0$ and $\langle \xi_i(t)\xi_j(t') \rangle = \delta_{ij}\delta(t - t')$. Note that the reaction rates, $a_i$, are proportional to $N_S$ such that the internal noise items in the CLE scale as $1/\sqrt{N_S}$. In the macroscopic limit $N_S \rightarrow \infty$, the internal noise can be ignored and the system's dynamics is described by the deterministic eq 2. Apparently, the kinetics of system 3 relates to the cell size, $N_S$. In the following, we will mainly use the CLE as our stochastic model for numerical simulation. The PA algorithm is also used to show the consistence of the results.

## 3. Results and Discussion

To investigate the effect of internal noise, it is useful to view the corresponding deterministic kinetics as a comparison. To this end, we perform numerical calculation of eq 2 using the explicit Euler method with a time step of 0.01 s. The partial pressure of NO, $P_{NO}$, is chosen as a control parameter. With the variation of $P_{NO}$, the system undergoes steady state (SS), supercritical Hopf bifurcation (HB), and deterministic oscillation (DO). The bifurcation diagram is plotted in Figure 1. The HB point resides at h ($P_{NO} \simeq 3.044 \times 10^{-7}$ mbar), and deterministic oscillation occurs in the case $P_{NO} > 3.044 \times 10^{-7}$ mbar. Between the HB point (h) and $P_{NO} \simeq 4.71 \times 10^{-7}$ mbar (not shown) is the oscillatory region. (See ref 30 for bifurcation details.)

One knows that noise can play constructive roles only near the critical points. Therefore, in the present study, we focus on the effect of internal noise when $P_{NO}$ is tuned very close to the HB point (h) but inside the SS region. When the cell size is very large, the system would not sustain stochastic oscillations due to small enough noise intensity. However, when the number of sites becomes small, simulations via the CLE or the PA all allow "stochastic" oscillations due to moderate noise. Such stochastic oscillations are distinct from random noise in that there is a clear peak in the power spectrum. To compare with the deterministic kinetics, we have also plotted in Figure 1 the stochastic oscillation of CO coverage triggered by very small internal noise at $N_S = 10^8$. One can see that the HB point defined in the deterministic kinetics now disappears and stochastic oscillations occur in the case of deterministic steady states, which implies there is essential discrepancy between deterministic and stochastic kinetics, and one cannot qualitatively distinguish the SS region and the oscillation region from the time behavior only.

Now we turn to numerical simulation of stochastic system 3. Simulations show that the stochastic oscillations are noticeably influenced by cell size, $N_S$. Although the oscillation amplitude decreases monotonically with increasing $N_S$, the regularity and relative intensity of stochastic oscillation is changing non-monotonically. When $N_S$ is small ($<10^4$), the large amplitude stochastic oscillation is quite noisy and the oscillation signal is almost smeared by large internal noise (not shown); as $N_S$ increases to $\sim 5 \times 10^4$, the oscillation becomes a little regular (top of parts a and b of Figure 2) and a weak oscillation signal appears in the corresponding power spectrum density (PSD) (dashed line in Figure 3). When $N_S$ increases to an intermediate value ($\sim 10^5$), the oscillation exhibits a little better performance; as $N_S$ increases to $\sim 6 \times 10^5$, the performance becomes the best (middle of parts a and b of Figure 2) and the oscillation intensity is the strongest (dotted line in Figure 3). However, as $N_S$ further increases ($\sim 10^6$), the performance get worse (bottom of parts a and b of Figure 2) and the oscillation intensity falls again (solid line in Figure 3). Figure 4 displays the variations of oscillation frequency and global reaction rate (GRR) of $a_6$ with changing $N_S$. One can see that the frequency changes little and the GRR changes slightly when $N_S > 1.5 \times$

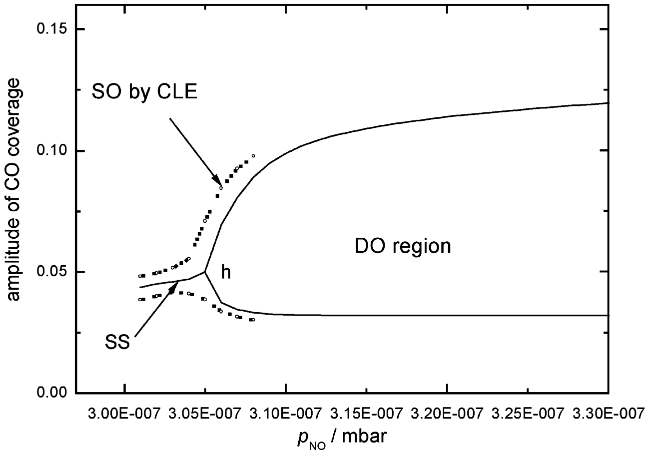

**Figure 1.** Bifurcation diagram of CO coverage for the deterministic equations (eq 2). The HB value is about $P_{NO} \simeq 3.044 \times 10^{-7}$ mbar. The symbols SS, h, and DO denote steady state, supercritical HB, and deterministic oscillation, respectively. For comparison, stochastic oscillation (SO) with an extremely small amplitude induced by a very small internal noise at $N_S = 10^8$ is also plotted.

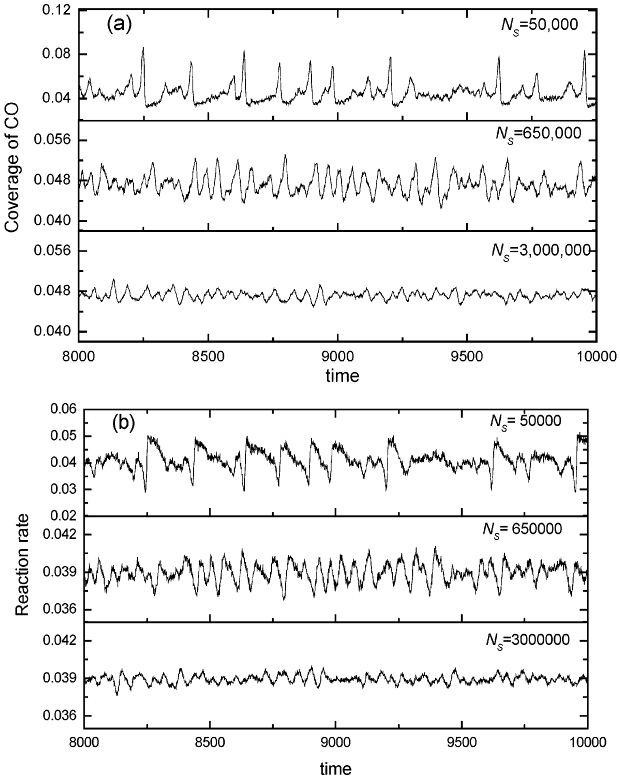

**Figure 2.** Oscillation time series of CO coverage (a) and reaction rate (b) for three values of cell size, $N_S$, at $P_{NO} = 3.032 \times 10^{-7}$ mbar.

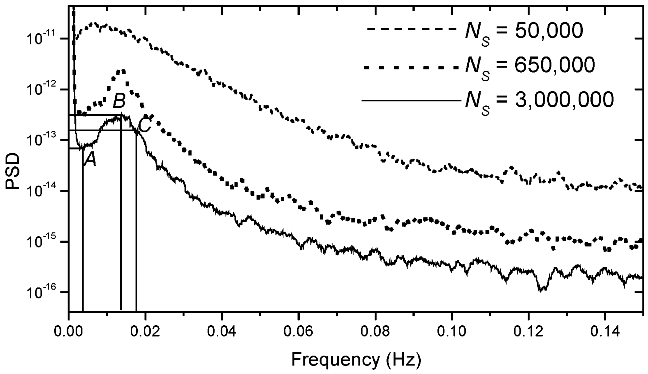

**Figure 3.** Smoothed power spectra for the stochastic oscillation of reaction rate $a_6$ for three different typical cell sizes, $N_S = 5 \times 10^4$, $6.5 \times 10^5$, and $3 \times 10^6$, respectively. The control parameter is $P_{NO} = 3.032 \times 10^{-7}$ mbar. The points *A*, *B*, and *C* in the PSD curve for $N_S = 3 \times 10^6$ demonstrate how to calculate the effective SNR, $\beta = [P(B)/P(A)] \times \omega_B/(\omega_C - \omega_B)$, where point *C* is located by the condition $P(C) = P(B)/e$, here $P(\cdot)$ denotes the power spectrum density (PSD) for a given frequency. Note that an arbitrary unit is used for the PSD.

$10^5$. Interestingly, although internal noise noticeably alters the oscillation waveform of reaction rate $a_6$ (see Figure 2b), it nearly does not influence the value of the GRR. This peculiar phenomenon may be attributed to the nature of continuous HB involved in the system, where the reaction rates oscillate symmetrically and homogeneously around the unstable steady state in the vicinity of the HB point (h).

The performances of spectra in Figure 3 already foretell the existence of optimal internal noise which would favor the reaction oscillations. To quantitatively measure the relative performance of the stochastic oscillations, we have calculated the effective SNR[24,25] by the simulations of the CLE and the PA algorithms. The definition of effective SNR is described in the caption of Figure 3. The obtained effective SNR as a function of cell size at $P_{NO} = 3.032 \times 10^{-7}$ mbar are plotted in Figure 5a. A clear maximum is present for $N_S \simeq 6.5 \times 10^5$, which indicates the existence of a resonance region and the occurrence of *internal noise SR* (INSR). Two results obtained by both algorithms are in good qualitative agreement.

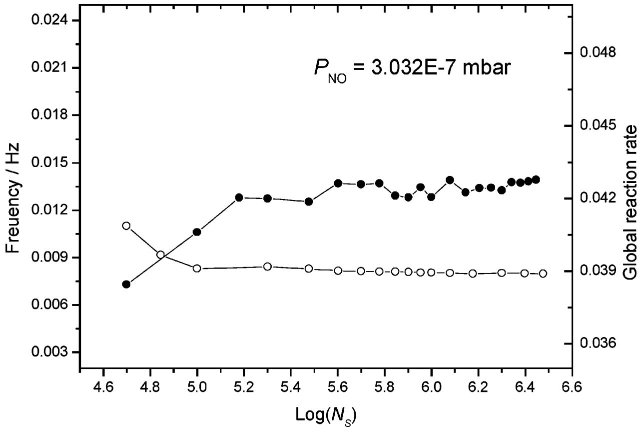

**Figure 4.** Frequency (filled circles, left axis) and GRR (open circles, right axis) versus $N_S$. They change little with the increase of $N_S$.

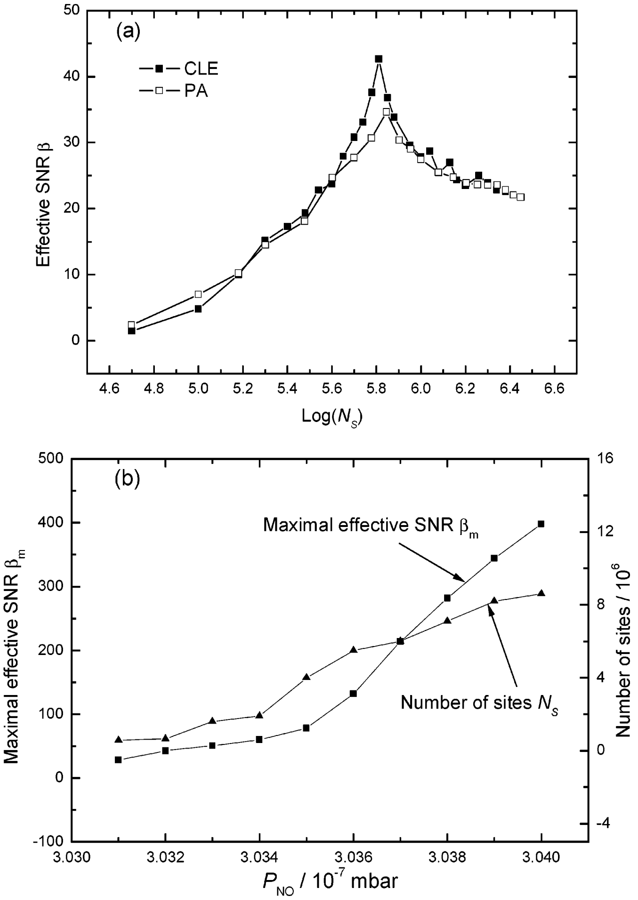

**Figure 5.** (a) Variation of the effective SNR, $\beta$, as a function of $N_S$. A maximum of SNR is present for $N_S \simeq 6.5 \times 10^5$, implying the occurrence of internal noise SR. (b) Maximal effective SNR, $\beta_m$, and corresponding cell size, $N_S$, as a function of $P_{NO}$. They increase with increasing $P_{NO}$ toward the HB point (h).

Using the CLE, we have also performed simulations of system 3 for other values of $P_{NO}$ to study how the INSR behavior depends on the value of the control parameter. Similar phenomena but with a shift of $N_S$ and of maximal SNR with changing $P_{NO}$ are found, as shown in Figure 5b. With increasing

$P_{NO}$ toward the HB point, both the value of $N_S$ for maximal SNR and the value of maximal SNR become larger.

The occurrence of INSR demonstrates the important roles of internal noise in such a small scale surface catalytic reaction inside one single cell on a single crystal surface. Generally, internal noise is believed to always play destructive roles and would be resisted by the system. However, the INSR reveals that the reaction oscillations can be quite robust to the variation of external parameters due to the onset of intrinsic stochastic oscillations induced by internal noise. On the other hand, instead of trying to resist the internal noise, the system may also exploit it to enhance the oscillation performance via the tuning of internal noise.

Note that, despite its slight effect on both the GRR and oscillation frequency within a broad range of $N_S$, internal noise has influenced drastically the regularity and relative intensity of stochastic oscillations indicated by apparent variation of SNR. Although it is not clear at present how regularity would play a function in reaction activity, there would be inherent relations between them by which internal noise would favor chemical reactions.

Now we move to a simple discussion on the cell sizes related to the occurrence of stochastic oscillations and to the maximal SNR. Simulations show that the site number for the onset of stochastic oscillations is $\sim 10^7$ and for the maximal SNR about $N_S \simeq 6.5 \times 10^5$ (approximately equivalent to $0.2 \times 0.2\ \mu m^2$ on Pt(100) in the case of an adsorption site concentration of $1.3 \times 10^{15}/cm^2$). Since the coverage of CO in the oscillation of best performance is around $\sim$0.05 ML (see Figure 2a), the reacting molecule population of CO is thus nearly $\sim 10^4$, which are somewhat different compared to the catalytic CO oxidation on the Pt tip where noise-induced spikelike oscillations could only be obtained for $N \leq 10^4$ and internal noise became significant only in a single cell with, for example, the 20 Å × 200 Å area.[3] It may be due to the substantially distinct oscillatory behaviors in these two reactions. In the catalytic CO oxidation, relaxation oscillations with a large amplitude of spikelike form are present, which are caused by larger internal noise. Since in the NO + CO reaction under consideration the system exhibits oscillations with a small amplitude when the control parameter $P_{NO}$ passes across the supercritical HB, the internal noise needed for triggering and enhancing is relatively small in contrast to the catalytic CO oxidation. In addition, for the NO + CO reaction, the desorption rates of CO and NO are assumed to be largely dependent on the coverage of CO and NO and the dissociation rate of NO on those of CO, NO, and oxygen atoms as well. Such a higher nonlinearity of the system would give rise to its higher sensitivity to coverage fluctuations. This may be another reason for the considerable difference in cell size for the two systems. This also implies that the fluctuations would play more important roles in the present reaction system. The present result has again demonstrated the important and crucial roles of internal noise.

One should note that the present work actually applies a new idea to study the NO + CO system on a single crystal surface. As compared to our previous work in ref 33, the present work accounts for the internal noise, which has a distinct nature from the external one, and a stochastic model has been constructed. While compared to the work in ref 27, we consider a single crystal surface here, which is divided into small well-mixed cells, rather than a nm-particle, and the system is also different. Therefore, the present work provides a second, different example of the important effect of internal noise.

## 4. Conclusion

In conclusion, we have studied the influence of internal noise on the NO + CO reaction in a well-mixed cell over Pt single crystal surfaces using the chemical Langevin equations and the Poisson approximation algorithm. It is shown that the coverage fluctuations can induce oscillations and, most importantly, the performance of the internal noise-induced stochastic oscillations undergoes a maximum with variation of the internal noise level ($N_S \sim 10^5$), which demonstrates the occurrence of INSR. The INSR demonstrates that there is an optimal internal noise level which would favor the reaction oscillations of NO reduction by CO with respect to relative oscillation performance. Similar results for different values of NO partial pressure are obtained, but the cell size for maximal SNR and the value of maximal SNR increase with increasing $P_{NO}$, which represents the robustness of the INSR to external parameters and the influence of NO pressure on the kinetics. From the previous study of internal noise roles in CO oxidation on nanometer-sized Pd particles and the present result, we may draw a conclusion that the internal noise effect seems to be *universal* for such small scale surface catalytic reaction systems. These findings may reveal the great importance of internal noise in mesoscopic surface catalytic reactions.

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