Optimal Particle Size for Reaction Rate Oscillation in CO Oxidation on Nanometer-Sized Palladium Particles

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Based on a mesoscopic stochastic model, we have studied the effect of particle size in the catalytic oxidation of CO on nanometer-sized palladium particles, using chemical Langevin equations. The reaction rate oscillations are of a stochastic nature, because of considerable internal noise in such mesoscopic systems. The performance of the stochastic oscillations undergoes a maximum with the variation of the particle size at a given CO partial pressure, which demonstrates the occurrence of *particle size resonance*. Such a phenomenon is robust to the change of CO pressure, except for some quantitative discrepancies. These results imply that there exists an *optimal particle size* for the CO oxidation over nanometer-sized supported palladium particles.

1. Introduction

Particle size effects in the reaction kinetics of heterogeneous catalysis on nanometer-sized catalyst particles have attracted much attention in the past decades.[1-4] It is widely accepted that the atomic structure and electronic properties are the main reasons for the peculiar kinetics on nanometer-sized particles. The influence of particle size on the catalytic activity is the most extensively studied subject. It was observed that particle size may drastically change the catalytic activity (i.e., the "turnover rate"), varying in different ways with increasing size, depending on the different types of "structure sensitivity".[1] It was shown experimentally[5] and theoretically[6] that essential differences in the catalytic activity exist between an extended surface and a nanometer-sized cluster. Studies have found that the particle size between a few nanometers and <30 nm is especially interesting, because, in this case, the nanometer-sized metal particles are sufficiently large to have developed the bulk electronic structure but small enough to exhibit size-related kinetic effects.[6] Approximately, the peculiar reaction behavior on nanometer-sized particles may be classified as three types. The reaction kinetics is mainly affected by the electronic factor for clusters or very small metal crystallites with $d < 4$ nm, and by particle structure for crystallites with 4 nm $< d <$ 10 nm in diameter; for $d >$ 10 nm, because of the possible reactions that occur on facets, the kinetics on the facets are expected to be the same as those for the corresponding single-crystal surfaces, although the edges may, of course, be important as well.[6]

Despite these successes in the understanding of the dependence of catalytic kinetics on the particle size, there is another important type of particle size effect on such heterogeneous catalytic reactions. Namely, for chemical reactions that occur on the surface of such a small particle, *internal noise* that is due to the stochastic nature of the reaction events may become considerable. It is generally accepted that the strength of the internal noise scales as $1/\sqrt{\Omega}$, where Ω is some type of extensive parameter proportional to the size of the reaction space (here, it is the number of active adsorption sites on the particle surface). One already knows that a variety of nonlinear dynamic behaviors, such as reaction rate oscillations (RROs) and chemical waves, have been observed on heterogeneous catalytic reaction systems, including the CO oxidation on platinum single-crystal surfaces and on palladium surfaces.[7-9] Therefore, an interesting and intriguing question naturally arises: how would the internal noises influence the nonlinear dynamics on nanometer-sized catalyst particles? Since the strength of the internal noise is determined by the particle size, the answer of this question would also uncover the effect of particle size, from a nonlinear dynamic point of view instead of a quantum mechanics point of view.

Only recently has attention been given to the effect of internal noise in catalytic reaction over single-crystal surfaces and nanometer-sized catalyst particles. It was observed that internal noise can induce transitions between the active and inactive branch of the reaction for catalytic CO oxidation on a platinum field-emitter tip.[10] Internal noise becomes essential in the dynamic behavior of CO oxidation when surface cells over low-index single-crystal surface are very small.[11] In the study of spatiotemporal self-organization in catalytic oxidation of hydrogen on Pt(111), the authors also suggested that a mesoscopic stochastic model that takes internal noise into consideration should be used to explain the experimental observations quantitatively.[12] Using a stochastic model, Peskov and co-workers[13-15] 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. These works provide clear information that internal noise might have a crucial role in the catalytic reactions on nanometer-sized particles, which also elucidates the crucial effects of particle size.

Here, in the present paper, we report the nontrivial effect of particle size on CO oxidation over nanometer-sized palladium (Pd) particles. We have studied how the RRO observed in such a system is influenced by the internal noise that is inherent in

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RRO in CO Oxidation on Pd Particles

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TABLE 1: Stochastic Processes and Transition Rates for CO Oxidation over Nanometer-Sized Palladium Particles[a]

stochastic processes	reaction rate
$N_{CO} \rightarrow N_{CO} + 1$	$a_1 = k_1 P_{CO}(1 - x - y)N_S$
$N_{CO} \rightarrow N_{CO} - 1$	$a_{-1} = k_{-1} \exp(\epsilon_1 x)x N_S$
$N_O \rightarrow N_O + 2$	$a_2 = k_2 P_{O_2} \exp(-\alpha z)(1 - x - y)^2 N_S$
$(N_{CO}, N_O) \rightarrow (N_{CO} - 1, N_O - 1)$	$a_3 = k_3 \exp(-\beta w)xy N_S$
$(N_O, N_{O*}) \rightarrow (N_O - 1, N_{O*} + 1)$	$a_4 = k_4 \exp(\epsilon_4 x)y(1 - z)N_S$
$(N_O, N_{O*}) \rightarrow (N_O + 1, N_{O*} - 1)$	$a_{-4} = k_{-4}(1 - y)z N_S$

[a] Note: Parameter values at $T = 503$ K are $\alpha = 10$, $\beta = 10$, $\delta = 2311.2$, $k_1 = 250$ s^{-1} Torr^{-1}, $k_{-1} = 6$ s^{-1}, $k_2 = 350$ s^{-1} Torr^{-1}, $k_3 = 2000$ s^{-1}, $k_4 = 0.003$ s^{-1}, $k_{-4} = 0.01$ s^{-1}, $\epsilon_1 = 2.5$, $\epsilon_4 = 2.5$, and $P_{O_2} = 160$ Torr. See ref 14 and references therein for more details.

such a small chemical reaction system. Interestingly, we find that there is an optimal particle size where the oscillation is the most regular, demonstrating the occurrence of *particle size resonance* (PSR). It reveals that appropriate internal noise associated with appropriate particle size would be a benefit to the CO oxidation. We also show that this phenomenon is quite robust to the change of external parameters, such as CO partial pressure.

2. Model

The model used in the present paper was developed by Peskov et al.[14] for the oxidation of CO over a nanometer-sized palladium particle. The reaction proceeds via a Langmuir−Hinshelwood (LH) mechanism, including the adsorptions of CO and oxygen, the desorption of CO, the reaction of adsorbed CO and adsorbed oxygen, the diffusion of adsorbed oxygen on the surface into the subsurface, and the diffusion of the subsurface oxygen back to the surface. The dynamic state of a particle can be described by the number of adsorbed CO molecules (N_{CO}), the number of O atoms on the surface (N_O), and the number of O atoms on the subsurface (N_{O*}). The dynamics of the system is then described by stochastic birth−death processes that govern the change of these numbers. For the present model, the elementary processes and their transition rates are listed in Table 1, where $x = N_{CO}/N_S$, $y = N_O/N_S$, and $z = N_{O*}/N_S$ denote the respective concentrations of the reactants. N_S is the number of Pd atoms on the particle surface, N_b is the total number of Pd atoms in the particle body, and s is the fraction of surface sites ($s = N_S/N_b$). For simplicity, the particle is supposed to be a regular octahedron, such that one has $N_S = 6 + 4N_d(N_d - 2)$ and $N_b = N_d(2N_d^2 + 1)/3$ (here, N_d is the number of atoms in the diagonal of the particle ($N_d = (d/a) + 1$), d is the diagonal length of the particle, and a is the crystal constant of palladium ($a = 0.389$ nm). The variable w is a parameter that is used to describe the degree of bulk oxidation ($w = P_{O_2}(P_{O_2} + \delta s P_{CO})^{-1}$, where $\delta = k_{-5}/k_5$). We choose d as the parameter to denote the size of the particle.

In the case of $N_S \rightarrow \infty$ ($d \rightarrow \infty$), the internal noise can be ignored and the time evolution of the reactant concentrations can be described by the following deterministic equations:

$$\frac{dx}{dt} = \frac{a_1 - a_{-1} - a_3}{N_S}$$

$$\frac{dy}{dt} = \frac{a_2 - a_3 - a_4 + a_{-4}}{N_S}$$

$$\frac{dz}{dt} = \frac{a_4 - a_{-4}}{N_S} \quad (1)$$

However, for a catalyst particle a few nanometers in diameter, such a deterministic description is not strictly valid, because of

the existence of considerable internal noise. Basically, one should describe the system's dynamics by a chemical master equation, which describes the time evolution of the probability of having a given number of molecules/atoms (N_{CO}, N_O, and N_{O*}). There is no general procedure to solve this master equation analytically; however, it does provide the starting point for numerical simulations. Recently, Gillespie found that, under certain circumstances, it is also reasonable to approximate the master equation by a chemical Langevin equation (CLE).[16] Given the stochastic processes shown in Table 1, the CLE for the current model reads as follows:

$$\frac{dx}{dt} = \frac{1}{N_S}[(a_1 - a_{-1} - a_3) + \sqrt{a_1}\xi_1 - \sqrt{a_{-1}}\xi_{-1} - \sqrt{a_3}\xi_3]$$

$$\frac{dy}{dt} = \frac{1}{N_S}[(a_2 - a_3 - a_4 + a_{-4}) + \sqrt{a_2}\xi_2 - \sqrt{a_3}\xi_3 -$$
$$\sqrt{a_4}\xi_4 + \sqrt{a_{-4}}\xi_{-4}]$$

$$\frac{dz}{dt} = \frac{1}{N_S}[(a_4 - a_{-4}) + \sqrt{a_4}\xi_4 - \sqrt{a_{-4}}\xi_{-4}] \quad (2)$$

where $\xi_i(t)$ ($i = \pm 1, 2, 3, \pm 4$) 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 the reaction rates a_i are proportional to N_S, such that the internal noise items in the CLE scale as $1/\sqrt{N_S}$. The kinetics of the system described by eqs 2 relates to the particle size d via N_S and the bulk oxidation degree (w). In the following section, we will use the CLE to study the effects of the particle size d.

3. Results and Discussion

We numerically integrate eq 2 using the standard procedure for stochastic differential equations with a time step of 0.0001 s.[17] To begin, we keep $P_{CO} = 5$ Torr and set the particle size d to be a variable control parameter (other parameter values are given in Table 1). Stochastic RROs are observed for eq 2, which is distinct from random fluctuations in that there is a peak in their power spectra. Therefore, unlike the deterministic model, one cannot get a clear bifurcation diagram of the system described by eq 2 on the parameter d through stability analysis. Instead, one can only decide whether the stochastic oscillations exist or not through the sharpness of the peak in the power spectrum. Consequently, stochastic oscillations can only exist in a certain range of particle size (i.e., 2.5 nm $\leq d \leq$ 12 nm). If the particle size is <2.5 nm, the internal noise is too large, such that it smears any oscillatory information; if particle size is >12 nm, the internal noise is too weak, such that no stochastic oscillation can be "triggered".

The aforementioned discussion already seems to outline a picture of "resonance". Namely, it seems that the stochastic oscillation might show the best performance for an intermediate particle size inside the range. To demonstrate this, we have plotted the stochastic RRO for $d = 4$, 8, and 12 nm in Figure 1. It can be observed that the stochastic oscillation for a particle size of $d = 8$ nm is the most "regular". Correspondingly, the power spectra are drawn in Figure 2, where it is shown that the peak for $d = 8$ nm is the sharpest among the three, indicating the existence of an optimal particle size. Note that the power spectra curves are obtained by nearest averaging over 99 points from the original ones. We have used 16 384 data points, with an average time interval of 0.6 s, to calculate the power spectrum, and a Welch windowing function is used.[18]

To measure the relative performance of the stochastic oscillations quantitatively, we have defined an effective signal-
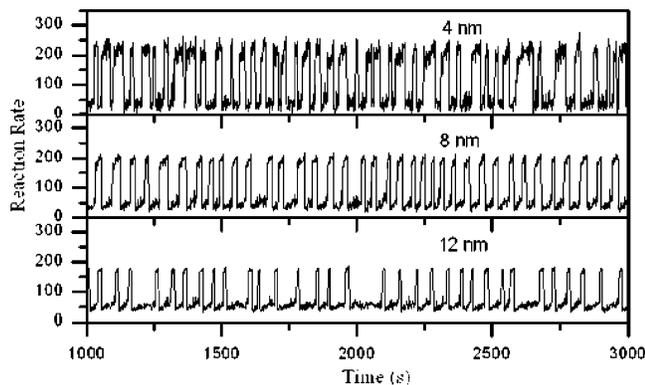
Figure 1. Stochastic reaction rate oscillations (RROs) for three typical particle sizes ($d = 4$, 8, and 12 nm) at $P_{CO} = 5$ Torr.
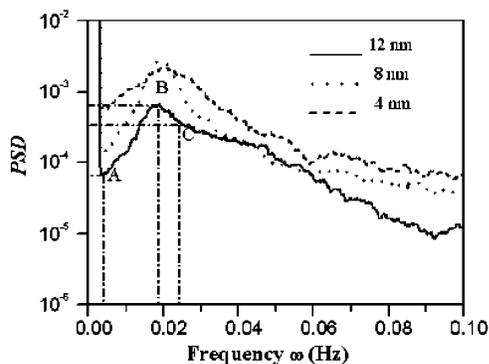

Figure 2. Corresponding smoothed power spectra for the time series shown in Figure 1. The points A, B, and C in the power spectrum density (PSD) curve for $d = 12$ nm demonstrate how to calculate the effective signal-to-noise ratio (SNR), i.e., $\eta = [P(B)/P(A)] \times \omega_B/(\omega_C - \omega_B)$, where point C is located by the condition $P(C) = P(B)/e$. Note that arbitrary units are used for the PSD.
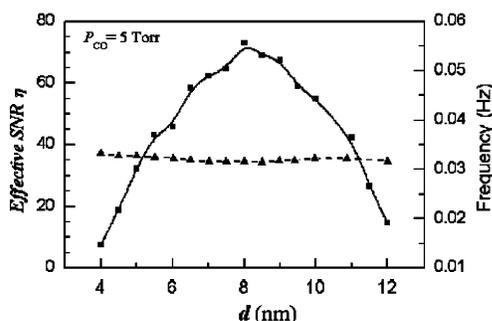

Figure 3. Dependence of effective SNR (left axis) on the particle size at $P_{CO} = 5$ Torr. The SNR passes through a maximum at $d \approx 8$ nm. The dashed line indicates the corresponding peak frequency (right axis).

to-noise ratio (SNR) as the height of the peak in the power spectrum, normalized by its relative width ($\eta = R/(\Delta\omega/\omega_P)$). Here, ω_P is the frequency at the peak, $\Delta\omega$ is the width between ω_P and the frequency ω_1 that satisfies the relation $\omega_1 > \omega_P$, and $P(\omega_1) = P(\omega_P)/e$ (where $P(f)$ denotes the power spectrum density (PSD) for a given frequency f); $R = P(\omega_P)/P(\omega_2)$, where $P(\omega_2)$ is the smallest PSD value between $P(0)$ and $P(\omega_P)$. (Also see the caption of Figure 2 for more details.) The dependence of η on particle size at $P_{CO} = 5$ Torr is plotted in Figure 3. A clear maximum is present at $d \approx 8$ nm, which evidently demonstrates the occurrence of PSR. For reference, the dependence of the corresponding peak frequency on the particle size is also displayed.

To check the robustness of the particle size resonance behavior, we have also performed similar studies for other values of P_{CO}; the results are shown in Figure 4. One sees that, for
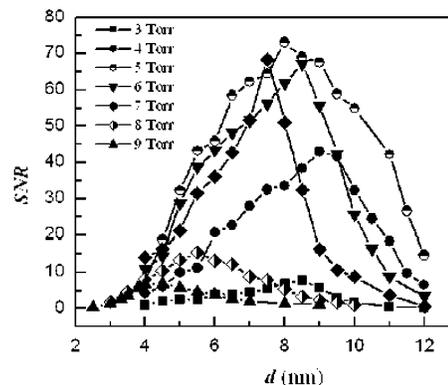

Figure 4. Dependence of the SNR on particle size for different P_{CO} values. The optimal particle size is dependent on the value of P_{CO}, and the maximum SNR value changes remarkably for different P_{CO} values.

P_{CO} values in the range of 3−9 Torr, the effective SNR undergoes a maximum with the variation of the particle size. However, values of the optimal particle size and the maximum SNR may show apparent discrepancies when P_{CO} changes. Interestingly, we find that the maximal SNR for $P_{CO} \approx 5$ Torr is much larger than that for larger or lesser P_{CO} values, showing that the stochastic oscillations show the best performance for an optimal particle size on one hand, and for an intermediate partial pressure of CO on the other hand.

We note that the result for RROs presented in this paper qualitatively agrees with the experimental result that the evolution of turnover rates goes through a maximum as a function of nm particle size.[1] Nevertheless, unlike the previous mechanism, in which the electronic factors had a key role, the present effect is caused by the *interplay of internal noise and nonlinearity* of the system. The existence of an optimal particle size demonstrates the important roles of internal noise in such small-scale dynamical systems. Actually, similar results have also been obtained in other mesoscopic chemical and biological systems.[19−25] It was reported that ion channel clusters of optimal sizes can enhance the encoding of a sub-threshold stimulus.[19,20] Shuai and Jung demonstrated that optimal intracellular calcium signaling appears at a certain size or distribution of the ion channel clusters.[21−23] In recent studies, we have shown that an optimal system size exists for stochastic oscillations in the Brusselator system and a circadian clock system.[24,25] All these results suggest that the optimal system size might be the *universal* characteristic for mesoscopic chemical or biochemical systems, and they also require that internal noise should be taken into careful account in the dynamics of such systems.

How can the optimal particle size (or PSR) have implications for CO oxidation on nanometer-sized palladium particles is still an open question. However, one point may be addressed. The existence of the PSR indicates that one should not only take into account internal noise in dynamics of CO oxidation on nanometer-sized particles but also carefully consider the effects of different internal noise strengths subjected to different nanometer-scale particle sizes. It still indicates that, for any a given CO partial pressure, the dynamical parameters of the system might have evolved to appropriate values to adapt to the particle size where the RRO would exhibit the best performance. We hope that our study can open more perspectives, especially experimental studies, in future works.

4. Conclusion

In summary, we have studied the particle size effect in the CO oxidation over a zeolite-supported nanometer-sized pal-

ladium particle, using the mesoscopic stochastic model and chemical Langevin equations. It is found that the performance of stochastic reaction rate oscillations (RROs) undergoes a maximum with the variation of the particle size, which demonstrates the occurrence of particle size resonance (namely, the existence of the optimal particle size). Similar phenomena for different CO pressures are obtained, showing the robustness of this effect to CO pressures. These results suggest that, at a given CO pressure, there exists an optimal particle size where the RRO would exhibit the best performance. The "optimal particle size" effect may imply the ubiquitous importance and constructive roles of internal noise in the catalytic oxidation over nanometer-sized supported catalyst particles.

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