Nonlinear Effects In Site Blocking Induced Oscillations

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Abstract

Higher order nonlinear effects of site blocking, which induces oscillations in the Monte Carlo simulation of CO oxidation, are outlined here. It is shown that the rate equations which include these effects exhibit a supercritical Hopf bifurcation in parameter domains where Monte Carlo simulations lead to oscillations.

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I. INTRODUCTION

Surface chemical reactions play an important role in the processes of heterogeneous catalysis, which are widely used in the chemical industry [1]. Monte Carlo simulation is a powerful tool for a microscopic description of these reactions [2,3]. Kinetic phase transitions, oscillations and chaos, pattern formation, and coupling between catalytic oscillators have been studied by the Monte Carlo method [4–7].

The oxidation of carbon monoxide \( CO \) is one of the most extensively studied surface catalytic reactions [8,9]. In a recent Monte Carlo study, an attempt of a mean field modeling was made for site blocking induced surface coverage oscillations [10]. The authors of Ref. [10] studied a mathematical model based on macroscopic rate equations for the characterization of oscillations seen in the Monte Carlo simulations. However, it was found that the mean field model does not lead to oscillatory dynamics in a parameter region where their Monte Carlo simulations show oscillations. In order to obtain oscillations, they numerically solved a part of their rate equations with data from the Monte Carlo simulation for dynamics of the free site and the inert molecule coverage. Such a combination of deterministic and stochastic time evolutions seems not to be satisfactory; it is more desirable to find a supercritical Hopf bifurcation in the model to ensure the occurrence and stability of oscillations. The aim of this work is to show that inclusion of high order nonlinear terms, which represent interactions inherent in this system, allows us to find oscillations within the rate equations. We find a Hopf bifurcation in the extended system, and we can determine the parameter domain for oscillatory dynamics.

II. SITE BLOCKING INDUCED OSCILLATIONS

The model system under study is the ZGB model [4], which is extended by the absorption and desorption of an inert molecule:

\[
\begin{align*}
CO_{gas} + \ast & \xrightarrow{w_1} CO_{ads}, \\
CO_{ads} & \xrightarrow{w_2} CO_{gas} + \ast, \\
O_2 + 2\ast & \xrightarrow{w_4} 2O_{ads}, \\
CO_{ads} + O_{ads} & \xrightarrow{w_5} CO_2 + 2\ast, \\
M_{gas} + \ast & \xrightarrow{w_6} M_{ads}, \\
M_{ads} & \xrightarrow{w_7} M_{gas} + \ast,
\end{align*}
\]

where \( ads \) indicates that the molecule is absorbed on the surface and \( gas \) indicates that the molecule is in the gas phase. \( \ast \) indicates a vacant site and \( M \) represents the site blocking inert molecule.

As was reported by Jansen and Nieminen [10], one can observe sustained coverage oscillations in the Monte Carlo simulations of Eqn. (1). In Fig. 1 we show results of our Monte Carlo simulation for these coverage oscillations. All variables and time are dimensionless in this paper. As compared with Ref. [10], we have used a different set of parameters to show that these oscillations can be observed in wide range of parameters. To improve the numerical performance we have implemented \textit{lists} in our Monte Carlo simulations. Separate lists
for the locations of free sites, CO, and inert molecules were updated during the simulations. For example, for an adsorption of a chosen adsorbent, a site was randomly selected from the list of free sites; for a desorption, a site was randomly selected from the corresponding list of CO or M.

The authors of Ref. [10] studied rate equations for a macroscopic characterization of the oscillations seen in the Monte Carlo simulation. The rate equations for the coverage of $CO_{ads}$, $O_{ads}$, and $M_{ads}$ are [10]:

$$\sigma = 1 - x - y - z,$$

$$\dot{x} = w_1 \sigma - w_2 x - 4w_3 xy,$$

$$\dot{y} = 4w_4 \sigma^2 - 4w_3 xy,$$

$$\dot{z} = w_5 \sigma - w_6 z,$$

where $\sigma$ is the free site coverage. It is known that Eqn. (2) shows oscillations in a narrow parameter domain [11], however, temporal pattern of these oscillations are very different from the oscillations seen in Monte Carlo simulations as shown in Fig. 1. It was found that Eqn. (2) does not show oscillations in the parameter domain where Monte Carlo simulations lead to oscillations. To obtain oscillations, the authors of Ref. [10] used data for $\sigma$ and $z$ from the Monte Carlo simulation. We suppose that the reason why Eqn. (2) does not show oscillations in the parameter domains of interest is that it does not include important higher order nonlinear effects inherent in Eqn. (1), which are essential for oscillations shown in Fig. 1.

### III. HIGHER ORDER NONLINEAR EFFECTS

Monte Carlo simulations of Eqn. (1) suggest that two nonlinear effects are crucial for oscillations in this system. They destabilize $O$ and CO rich surfaces, correspondingly.

In Fig. 2 we show snapshots of the surface at two different time moments. Fig. 2a corresponds to the time moment when there are no $CO_{ads}$ molecules left on the surface. Note that in the original ZGB model, for the parameters we have chosen, the system goes to the state fully covered by $O_{ads}$ [4]. However, the presence of the inert molecules shown in Fig. 2a as the brightest spots, prevent such a fully $O_{ads}$ covered state. Moreover, these inert molecules allow for the presence of enough vacant sites; these are shown as black areas in Fig. 2. In these vacant areas, CO molecules can be absorbed; their coverage can grow if they are isolated by the inert molecules from $O_{ads}$ covered areas. By taking into account this nonlinear effect, which includes interaction among $CO_{ads}$, $O_{ads}$, and $M_{ads}$, the reaction term in Eqn. (2) can be modified as $4w_3 xy(1 - \kappa z)$, where $\kappa$ is the blocking coefficient.

Fig. 2b shows nucleation of the $O_{ads}$ covered state on the $CO_{ads}$ rich surface. As an adsorption of $O_2$ requires two free sites, nucleation of the $O_{ads}$ island may seem an unlikely process, if one starts from the fully $CO_{ads}$ covered state as an initial condition. However, there is another nonlinear effect which may lead to explosive growth of an $O_{ads}$ island. Suppose that the desorptions of two $CO_{ads}$ molecules have vacated a pair of adjacent sites. On these sites, $O_2$ can be absorbed, and if this happens, $CO_{ads}$ and $O_{ads}$ will immediately react. As the surface is rich with $CO_{ads}$, the reaction will free four sites. On these four sites, two $O_2$ molecules can be absorbed. This cascade may lead to explosive growth of the $O_{ads}$
island. Therefore, there is another nonlinear effect which is particularly noticeable during a nucleation of an \( O_{ads} \) island on a \( CO_{ads} \) rich surface. In the lowest order of nonlinearity, due to the nonlinear increase of available adjacent free sites through the reaction, the growth of \( O_{ads} \) can be termed as \( 4\omega w_3 x^2 y \), where \( \omega \) is the coefficient for the nonlinear growth of adjacent free sites. We verified that \( 4\omega w_3 x^2 y^2 \) can also serve well for this term.

The two nonlinear effects manifest themselves randomly in Monte Carlo simulations. For a macroscopic description, we consider them deterministic processes. Thus, Eqn. (2) can be modified into the form:

\[
\begin{align*}
\dot{x} &= w_1 \sigma - w_2 x - 4w_3 xy(1 - \kappa z), \\
\dot{y} &= 4w_4 \sigma^2 - 4w_3 xy(1 - \omega x), \\
\dot{z} &= w_5 \sigma - w_6 z.
\end{align*}
\tag{3}
\]

We want Eqn. (3) as simple as possible. We include the reaction term \( 4w_3 \kappa x y z \) in the first equation only because its effect in the second equation is assumed to be small. This assumption stems from a microscopic process: a pair of \( O_{ads} \) can not be blocked by a single inert molecule. The reason why we include \( 4w_3 \omega x^2 y \) in the second equation only is also taken from a microscopic fact: for the adsorption of \( CO \), the presence of two free adjacent sites is not essential.

We note that the two effects were also described by Jansen and Nieminen [10]; however, they did not include them explicitly in the rate equations. We also note that Eqn. (3) is much simpler than the rate equations in the pair approximation of Eqn. (1), which do not show oscillations in the parameter range of interest [11]. Eqn. (3) is an approximate model, and it is desirable to derive it systematically.

IV. A HOPF BIFURCATION

Because of its nonlinear terms, analytic treatment of Eqn. (3) is difficult. Nevertheless, it can be studied numerically. For example, one may use the software "XPPAUT" by B. Ernoutrout [12].

We found that for the occurrence of a Hopf bifurcation it is not necessary that both \( \kappa \) and \( \omega \) were nonzero in Eqn. (3). However, we found that parameter space for oscillations are larger if both \( \kappa \) and \( \omega \) are nonzero.

A. case \( \kappa \neq 0 \) and \( \omega \neq 0 \)

In the present case, it is difficult to find analytic expressions for the steady states of Eqn. (3). In Fig. 3 we show a numerical integration of Eqn. (4). Here, in contrast to its dynamics shown in Fig. 1, the inert molecule concentration remains high. We suppose that the main reason for this is that \( w_3 \) is finite in Fig. 3, but \( w_3 = \infty \) in Fig. 1. Also, a better choice of the rate constants can be made in order to compare dynamics in the rate equations and Monte Carlo simulations [2].

A Hopf bifurcation in this system is shown in Fig. 4. Thus, the nonlinear effects we outlined in the previous section may indeed lead to stable oscillations. A two parameter
bifurcation diagram is shown in Fig. 5. We found that with the increase of $w_3$, the parameter region for a Hopf bifurcation widens. We found that such an increase is accompanied by the emergence of saddle nodes.

**B. case $\kappa \neq 0$ and $\omega = 0$**

In the present case, the steady states are given by,

$$x_0 = w_2^{-1}(w_1z_0 - 4w_4z_0^2 + 4\kappa w_4z_0^3),$$
$$y_0 = 1 - x_0 - 2z_0,$$

where $z_0$ is a solution to

$$w_2^2w_4z_0 + w_3(w_1 + 4w_4z_0(\kappa z_0 - 1)) = 0.$$  

Once again we were able to analyze stability of $x_0, y_0$ and $z_0$ numerically only. Oscillations for the present case are shown in Fig. 6. We note that in the present case, except the Hopf bifurcation, saddle node bifurcations occur in the system.

**C. case $\kappa = 0$ and $\omega \neq 0$**

As in the previous case, the steady states of Eqn. (3) can be expressed through a polynomial. Again, we were able to solve the polynomial numerically only. As a result, a linear stability analysis of these steady states has turned out to be difficult. Numerically detected oscillations for the present case are shown in Fig. 7. Note the exceptions of $w_3$’s value and $\omega \neq 0$; these are the reaction rates used in Ref. [10] for Monte Carlo simulations. We note that for the parameters used in Fig. 6 - 7, a parameter domain for the Hopf bifurcation was smaller in the present case then it was in the previous case.

**V. DISCUSSIONS**

A microscopic study of a reaction system based on Monte Carlo simulations can reveal the molecular mechanisms of catalytic processes. As an example, in this work, such study has allowed us to outline the essential nonlinear processes in site blocking caused oscillations. However, fora more complete study of a reaction system, the role of diffusion should be taken into account [13]. In that sense, Eqn. (4) can be a useful starting point for a reaction diffusion study of site blocking induced oscillations. The preliminary results of a reaction diffusion system in one dimension, with a diffusion of $x, y,$ and $z$, show synchronous oscillations, stable long lived islands and diffusion induced chemical turbulence [14]. More detailed results on this, and its comparison to the Monte Carlo simulations, which include diffusion of adsorbents, will be reported elsewhere [15].

Finally, we suppose that the nonlinear effects and stable oscillations due to site blocking can be detected in experimental studies on $CO$ oxidation.
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FIGURES

FIG. 1. Coverage oscillations on the square lattice. Open circles: $\bar{\theta}_{CO_{ads}}$. Long dashed: $\bar{\theta}_{O_{ads}}$. Solid lines: $\bar{\theta}_{M_{ads}}$. Rate constants: $w_1 = 0.44$, $w_2 = 0.005$, $w_3 = \infty$, $w_4 = 0.56$, $w_5 = 0.004$, $w_6 = 0.004$. Time is scaled to the total number of sites $S = N^2$, $N = 256$. $\bar{\theta} = \frac{1}{S} \sum \theta_i, i = CO_{ads}, O_{ads}, M_{ads}$.

FIG. 2. Snapshots of the surface at two different moments. a.) A phase without $CO_{ads}$ coverage. b.) Emergence of an $O_{ads}$ island on the $CO_{ads}$ dominant surface. Parameters are the same as in Fig. 1.

FIG. 3. Coverage oscillations in Eqn. (3). Open circles: $x$. Long dashed line: $y$. Solid line: $z$. Parameters are the same as in Fig. 1 except $w_3 = 5$, $\omega = 1$, $\kappa = 2$.

FIG. 4. A Hopf bifurcation diagram. Solid line represents a stable steady state. Circles represent the Hopf bifurcation branch: filled circles show the supercritical Hopf bifurcation, open circles show unstable oscillations. Dashed and thin lines show an unstable steady state. Parameters are the same as in Fig. 3.

FIG. 5. A two parameter bifurcation diagram. Oscillations occur in the area marked by $osc$. Other parameters are the same as in Fig. 3.

FIG. 6. Oscillations in the case $\omega = 0$. Open circles: $x$. Long dashed line: $y$. Solid line: $z$. Parameters are: $w_1 = 0.2$, $w_2 = 0.01$, $w_3 = 5$, $w_4 = 1$, $w_5 = w_6 = 0.01$ and $\kappa = 5.5$.

FIG. 7. Oscillations in the case $\kappa = 0$. Open circles: $x$. Long dashed line: $y$. Solid line: $z$. Parameters are: $w_1 = 1$, $w_2 = 0.001$, $w_3 = 5$, $w_4 = 0.52$, $w_5 = w_6 = 0.0003$, and $\omega = 1$. 
Figure 1
Figure 2a-b
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7