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Kinetic oscillations on nm-sized catalyst particles: NO reduction by CO on Pt

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We present Monte Carlo simulations of kinetic oscillations in the NO–CO reaction occurring due to the interplay of catalytic steps including autocatalytic NO dissociation. The lattice size is varied from 100×100 to 10×10 in order to mimic nm-sized catalyst particles. More or less regular oscillations are found for the sizes down to 15×15. In combination with similar results obtained earlier for two other models describing CO oxidation accompanied by oxide formation and surface restructuring, this finding forms one of first firm quantitative ingredients of the theory of oscillatory kinetics on supported catalysts.

KEY WORDS: catalysis; models of surface chemical reactions; models of non-equilibrium phenomena; Monte Carlo simulations.

Periodic kinetic oscillations have been observed in many catalytic reactions occurring on single crystals, polycrystalline samples (foils, ribbons and wires) and supported catalysts with the catalyst-particle size down to a few nanometers [1–5]. Interpretation of such oscillations raises many interesting and non-trivial questions. One of them is *how are kinetic oscillations on a single supported catalyst particle depend on the particle size*? The response to this question can hardly be unique, because reaction kinetics on such particles in general and oscillatory reactions in particular can be complicated by many factors including interplay of the reaction kinetics on different facets, adsorbate-induced reshaping of catalyst particles, complex boundary conditions, reactant supply via the support, etc. [6,17]. Despite all these complications, the key point is that with decreasing particle size the number of reactants decreases, fluctuations increase, and accordingly the periodic kinetics should anyway eventually disappear. Quantitatively, this point can be clarified by using Monte Carlo (MC) simulations. The first simulations in this area should obviously be based on generic models with a minimal number of complicating factors. Practically, this means that it makes sense to focus attention on the simplest case of a uniform lattice of a small size.

Following this line, we executed MC simulations of oscillatory kinetics of CO oxidation by using the models incorporating oxide formation [8] and CO-induced surface restructuring [9]. The lattice size was varied from 50×50 to 5×5 in order to mimic nm catalyst particles. In both cases, more or less regular oscillations were found for the sizes down to 15×15. The specifics of CO oxidation and many other oscillatory reactions is that the oscillations result from the interplay of rapid catalytic steps and a relatively slow “side” process (e.g., surface restructuring). Oscillations including only catalytic steps may of course run as well. A good example is NO reduction by CO on Pt(100) (the mechanism of this reactions and the corresponding mean-filed (MF) and MC kinetic models are reviewed in Ref. [3] and in Section 8 of Ref. [5], respectively). At relatively high temperatures ($T > 450$ K), the complex behaviour of the NO–CO reaction is related to surface restructuring. At lower temperatures ($\simeq$420K), the oscillations are however believed to be entirely driven by an autocatalytic sequence involving NO dissociation under conditions where the surface is always in the (1×1) phase. In both cases, the details of the physics behind oscillations in this reaction are still open for debate (see reviews [3,5] and a recent paper [10]). The goal of this letter is to construct a MC model mimicking purely autocatalytic oscillations in the NO–CO reaction on Pt(100) and to show the model behaviour on the nm scale by decreasing the lattice size.

The conventional mechanism of NO reduction by CO on Pt is as follows:

$$\mathrm{CO_{gas}} \rightleftharpoons \mathrm{CO_{ads}}, \tag{1}$$

$$\mathrm{NO_{gas}} \rightleftharpoons \mathrm{NO_{ads}}, \tag{2}$$

$$\mathrm{NO_{ads}} \rightarrow \mathrm{N_{ads}} + \mathrm{O_{ads}}, \tag{3}$$

$$\mathrm{CO_{ads}} + \mathrm{O_{ads}} \rightarrow (\mathrm{CO_2})_{\mathrm{gas}}, \tag{4}$$

$$2\mathrm{N_{ads}} \rightarrow (\mathrm{N_2})_{\mathrm{gas}}, \tag{5}$$

$$\mathrm{NO_{ads}} + \mathrm{N_{ads}} \rightarrow (\mathrm{N_2O})_{\mathrm{gas}}. \tag{6}$$

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In reality, the adsorbed species participating in the steps above may occupy different sites and the ratio of the rates of different reaction steps is quite appreciable. Under such circumstances, it makes sense to construct a model in such a way that it is relatively simple and simultaneously mimics the key features of one of the probable scenarios of the reaction kinetics. Following this line, we neglect the N_2O-formation channel (6), because its rate is usually low compared to that of N_2 desorption (see [11] and references therein). In addition, we take into account that step (5) is rapid [11,12], the N coverage is low during oscillations, and accordingly N atoms can in simulations be simply removed from the lattice just after NO decomposition [11]. Adopting this approximation, we have on a lattice only NO and CO molecules and O atoms.

On Pt(100), NO and CO molecules may occupy different sites. This fact is however not central for interpretation of oscillations. For this reason, in our generic simulations, we use the simplest approximation including only one (top) type of sites on a square $L \times L$ lattice (earlier, this approximation was employed in many other theoretical studies treating the system under consideration). Lateral interactions between NO and CO molecules are neglected. As in reality, diffusion of these molecules is considered to be much faster than other processes.

O atoms are assumed to occupy hollow sites (i.e., the sites on the sublattice which is auxiliary to the main lattice) and accordingly do not block sites for NO and CO adsorption. To take into account that due to strong lateral repulsion between nearest-neighbour (nn) O atoms the saturation O coverage is usually fairly low (about 0.3 ML [12]), we prohibit oxygen adsorption on nn sites. Diffusion of O atoms is slow compared CO and NO diffusion, expected to be slow compared to other steps as well, and accordingly neglected (for discussion of experimental and theoretical data on oxygen diffusion on Pt, see Ref. [13]).

The Langmuir–Hinshelwood (LH) reaction (4) occurs between nn CO and O species.

The detailed data on the coverage dependence of the rate of NO dissociation on Pt(100) are lacking. In the simulations incorporating surface restructuring, this process is usually allowed if an NO molecule has a vacant nn site. Our experience indicates however that with no restructuring this approximation is not sufficient in order to get kinetic oscillations. For this reason, we introduce rapid decrease of the rate of NO dissociation with increasing coverages of all the species (see details below). The latter is agreement with quantitative data on NO dissociation on Rh (see a review [14]).

Taking into account that diffusion of adsorbed NO and CO molecules is fast, it is convenient to introduce the dimensionless parameters $p_{\rm rea}$ characterizing the relative rates of the catalytic cycle and diffusion. Specifically, these processes are run with probabilities $p_{\rm rea}$ and $1 - p_{\rm rea}$, respectively. The elementary reaction events are then performed by using the probabilities characterizing the relative rates of the reaction steps inside the catalytic cycle. With this specification, our MC algorithm is as follows.

(1) A random number $\rho\,(\rho \leq 1)$ is generated. If $\rho < p_{\rm rea}$, an adsorption–reaction trial is executed [item (2)]. For $\rho > p_{\rm rea}$, an CO- or NO-diffusion trial is performed [item (3)].

(2) An adsorption–reaction attempt contains several steps:
   (i) An adsorption site is chosen at random on the main sublattice, and a new random number ρ' is generated.
   (ii) If the site selected is vacant, CO or NO adsorption acts are realized provided that $\rho' < p_{\rm CO}$ and $p_{\rm CO} < \rho' < p_{\rm CO} + p_{\rm NO}$, respectively ($p_{\rm CO}$ and $p_{\rm NO}$ are the adsorption probabilities). If $\rho' > p_{\rm CO} + p_{\rm NO}$, the trial ends.
   (iii) If the site chosen is occupied by CO, CO desorption or LH-reaction trial is performed, respectively, for $\rho' < p^{\rm des}_{\rm CO}$ and $p^{\rm des}_{\rm CO} < \rho' < p^{\rm des}_{\rm CO} + p_{\rm LH}$ ($p^{\rm des}_{\rm CO}$ and $p_{\rm LH}$ are the desorption and reaction probabilities). For CO reaction, one of the nn sites is chosen at random on the auxiliary sublattice, and the trial is considered to be successful if the latter site is occupied by O. If $\rho' > p^{\rm des}_{\rm CO} + p_{\rm LH}$, the trial ends.
   (iv) If the site selected (site 1) is occupied by NO, NO desorption or decomposition is executed for $\rho' < p^{\rm des}_{\rm NO}$ and $p^{\rm des}_{\rm NO} < \rho' < p^{\rm des}_{\rm NO} + p_{\rm dec}$, respectively ($p^{\rm des}_{\rm NO}$ and $p_{\rm dec}$ are the corresponding probabilities). For NO decomposition, one of the nn sites (site 2) is chosen at random on the auxiliary sublattice, and the trial is considered to be successful if the latter site is vacant and has no O-occupied nn sites (the latter condition takes into account strong lateral repulsion between O atoms) and if two sites of the main lattice, which are nn both to site 1 and site 2, are vacant (due to this condition, the NO decomposition rate rapidly decreases with increasing NO and CO coverages). An O atom released during decomposition occupies site 2. A N atom is removed from the lattice [because step (5) is assumed to be rapid]. If $\rho' > p^{\rm des}_{\rm NO} + p_{\rm dec}$, the trial ends.

(3) For CO or NO diffusion, an adsorption site is chosen at random on the main sublattice. If the site is vacant, the trial ends. Otherwise, a nn site is randomly selected on the same sublattice, and if the latter site is vacant a CO or NO molecule changes its position.

All the MC runs were started from the clean surface and run with periodic boundary conditions. This approximation is reasonable if (i) the area of the face contacting the support is small and/or (ii) the activity of the boundary sites with respect to NO decomposition is not much higher than that of regular sites. [If condition (ii) holds, the dependence of oscillations on the type of the boundary conditions is weak.]

To measure time, we use MC steps (MCS). Usually, one MCS is defined as $L \times L$ MC trials. In our case, this definition would result in the time scale connected primarily with adsorbate diffusion, because this process is rapid compared to other steps. Our experience indicates however that the effect of adsorbate diffusion on the reaction kinetics is fairly weak, i.e., the results become to be nearly independent on the rate of diffusion, provided that this process is fast and the time scale is not directly related to its rate. Under such circumstances, the conventionally defined MC time is physically somewhat artificial (the situation here is similar to MF calculations where the time scale is usually independent of the rate of reactant diffusion). For this reason, we define one MC step as $L \times L$ MC trials of steps (1)–(5) on average. Practically, this means that the MC time is calculated by dividing the total number of trials by $L \times L$ and multiplying by $p_{\rm rea}$.

The model described is found to predict oscillations provided that the NO and CO impingement rates are nearly equal, NO and CO desorption are slow, and NO decomposition and LH step are fast com-

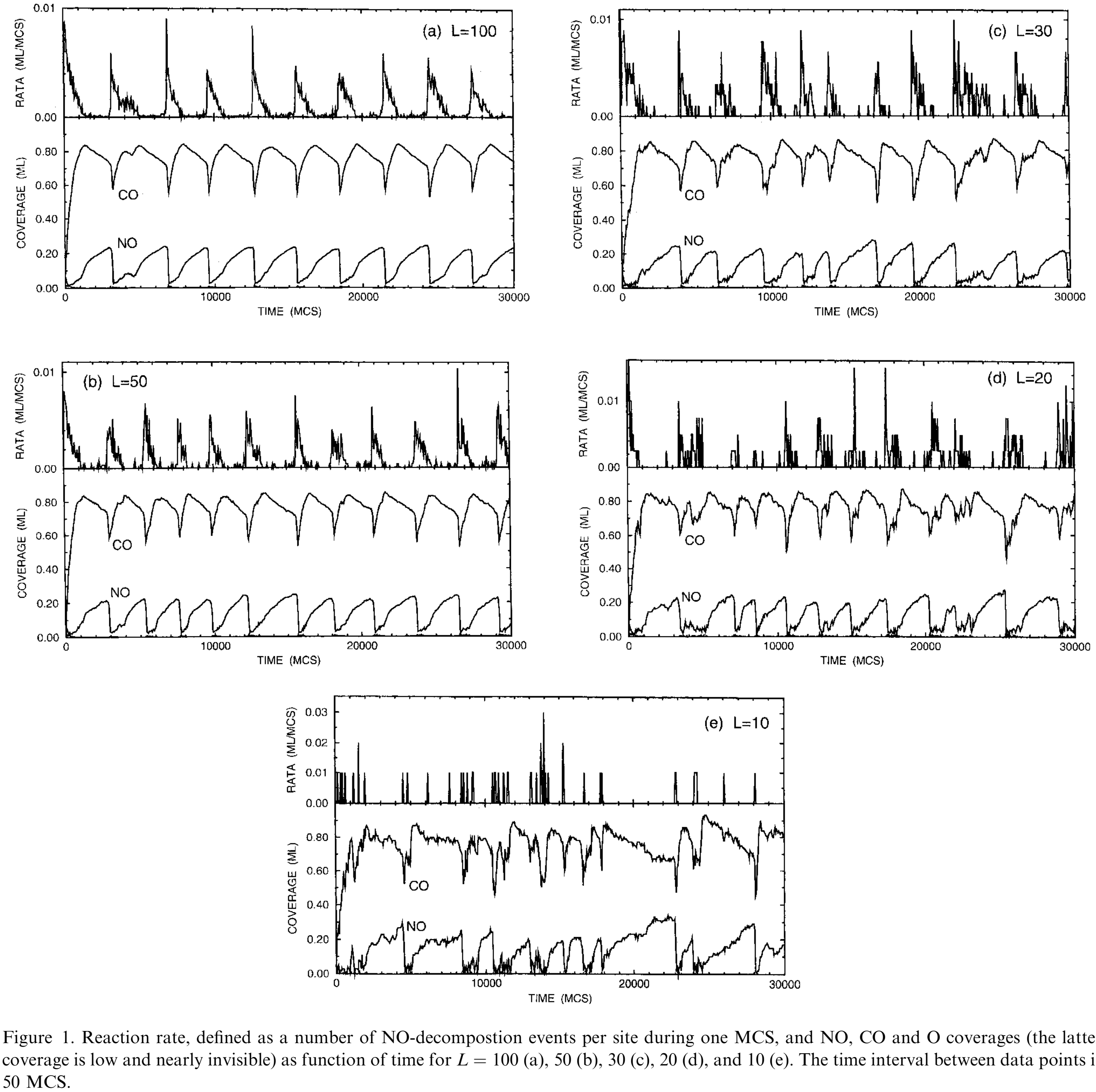
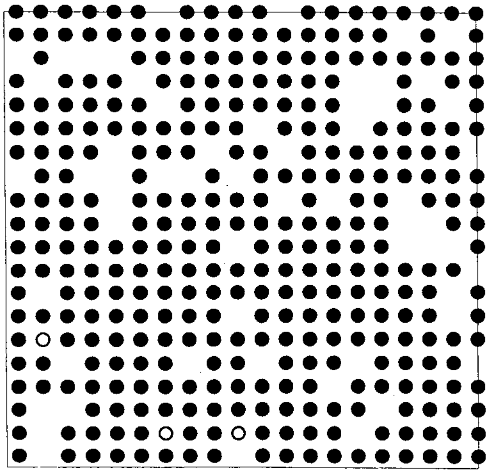


Figure 1. Reaction rate, defined as a number of NO-decompostion events per site during one MCS, and NO, CO and O coverages (the latter coverage is low and nearly invisible) as function of time for $L = 100$ (a), 50 (b), 30 (c), 20 (d), and 10 (e). The time interval between data points is 50 MCS.

(a) t=23400 MCS



(b) t=25450 MCS

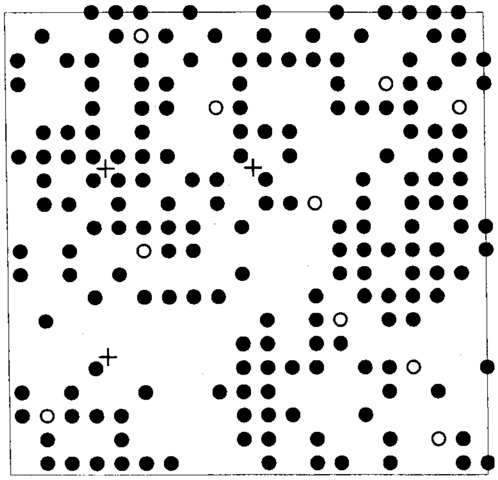


Figure 2. Typical snapshots of the lattice with $L = 20$ during the MC run shown in figure 1(d) at the points when the CO coverage is (a) maximum and (b) minimum. CO and NO molecules and O atoms are indicated by filled and open circles and plus signs, respectively. Vacant sites are not shown.

pared NO and CO adsorption. Typical oscillatory kinetics and lattice snapshots are shown in figures 1 and 2 for $p_{\rm rea} = 0.01$, $p_{\rm NO} = 0.01$, $p_{\rm CO} = 0.012$, $p^{\rm des}_{\rm NO} = p^{\rm des}_{\rm CO} = 0.0003$, $p_{\rm dec} = p_{\rm LH} = 1 - p^{\rm des}_{\rm NO}$, and $L = 100$, 50, 30, 20, and 10. The role of fluctuations is seen to increase with decreasing L. In particular, the oscillations become appreciably and completely irregular at $L = 20$ and 10, respectively.

In summary, our analysis of the model under consideration indicates that more or less regular kinetic oscillations can be observed down to $L \simeq 15$. For uniform lattices, this conclusion seems to be universal because our earlier simulations [8,19] indicate that it holds in the case of two other models as well. In combination, these findings form the first firm quantitative ingredient of our understanding of oscillatory kinetics on the nm scale.

Finally, it is appropriate to repeat that real kinetics on nm-sized catalyst particles can be complicated by many factors and some of them may make kinetic oscillations more irregular compared to those obtained on uniform lattices (see, e.g., Ref. [15]).

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