Comment on "Hysteresis phenomena in CO catalytic oxidation system in the presence of inhomogeneities of the catalyst surface"

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Scrutinizing the Monte Carlo algorithm, used by D.-Y. Hua and Y.-Q. Ma [Phys. Rev. E **66**, 066103 (2002)] in order to simulate the effect of defect sites on bistable kinetics of CO oxidation on single-crystal surfaces, we show that in their study (i) the rules for describing CO adsorption, desorption, and surface diffusion contradict the detailed balance principle and (ii) the ratio of the rates of CO diffusion and reaction between adsorbed CO and O species is opposite compared to that observed in reality.

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Rapid heterogeneous catalytic reactions are often bistable. A classical example here is CO oxidation on Pt. In this reaction, bistability has been observed on single crystals, polycrystalline samples, and supported catalysts at a pressure range from 10^{-12} bar to atmospheric pressure [1,2]. The understanding of this phenomenon is of considerable intrinsic interest and also important for rationalizing more complex reaction behavior (e.g., kinetic oscillations and pattern formation). In addition, the knowledge of the details of the bistable regimes of catalytic reactions is of practical significance (e.g., for optimization of the performance of automotive catalytic converters). For these reasons, the bistable kinetics of CO oxidation has long attracted attention of explorers working in different fields of physics and chemistry. The conventional approach to treating bistability is based on application of the mean-field kinetic equations [2,3] implicitly implying rapid diffusion of adsorbed species. More recent theoretical studies [4,5] focused on CO oxidation occurring on supported nanometer-sized catalyst particles rely on the Monte Carlo (MC) technique. The later technique has also been used by Hua and Ma (HM) [6] in order to demonstrate the role of randomly distributed defect sites in bistable kinetics of CO oxidation on single-crystal surfaces.

Our two comments concerning the MC algorithm employed by HM and the applicability of some their assumptions and conclusions to real systems are as follows.

(1) CO oxidation occurs via several steps including CO adsorption, desorption, and surface diffusion. The rate constants of these processes on defect sites may be different compared to those on regular sites. HM introduce defect sites of two types (1 and 2). The CO binding energy on these sites is assumed to be lower and higher respectively, than on the regular sites. The rate constant (or probability) of CO desorption from these sites $k_1^{\rm des}$ and $k_2^{\rm des}$ is accordingly considered to be higher and lower than that from regular sites $k_0^{\rm des}$. The rate constants (or probabilities) of CO adsorption on different sites $k_0^{\rm ads}$, $k_1^{\rm ads}$, and $k_2^{\rm ads}$, are set to be equal. CO diffusion is considered to occur via jumps to nearest-neighbor (nn) vacant sites. The rate constants (or probabilities) of jumps between different sites are assumed to be equal. In combination, these assumptions are not self-consistent, because they contradict the detailed balance principle. Application of this principle in MC and/or mean-field simulations of kinetic systems with reversible steps is general textbook wisdom, because otherwise the results of simulations are incorrect in situations close to detailed balance and may be incorrect in situations far from detailed balance. The important point is that the detailed balance principle is usually valid irrespective of whether a system is close to detailed balance or to chemical equilibrium (the system under consideration is always far from chemical equilibrium and far or close to the CO adsorption-desorption equilibrium during the high- or low-reactive regime when the surface is covered primarily by O or CO, respectively). For rate processes in adsorbed overlayers, the conditions of applicability of this principle depend on the rates of such processes as vibrational relaxation of adsorbed particles. These rates are well known to be extremely fast on the time scale of elementary reaction steps and diffusion jumps, and accordingly the detailed balance principle has to be fulfilled.

For regular sites and sites of type 1, for example, the detailed balance principle prescribes

$$\frac{k_0^{\rm ads}k_1^{\rm des}}{k_1^{\rm ads}k_0^{\rm des}}=\frac{k_{10}^{\rm dif}}{k_{01}^{\rm dif}}, \tag{1}$$

where $k_{10}^{\rm dif}$ and $k_{01}^{\rm dif}$ are the rate constants of CO jumps from a type-1 site to a nn regular site and back, respectively [note that the left- and right-hand parts of Eq. (1) contain ratio of the rate constants, and accordingly Eq. (1) holds despite the fact that diffusion is much faster than adsorption and desorption]. Taking into account that the rate constants of CO adsorption on different sites are considered to be equal (this assumption is reasonable), one can rewrite Eq. (1) as

$$\frac{k_1^{\rm des}}{k_0^{\rm des}}=\frac{k_{10}^{\rm dif}}{k_{01}^{\rm dif}}. \tag{2}$$

The latter relationship indicates that if desorption from defect sites of type 1 is faster than from regular sites (i.e., $k_1^{\rm des}>k_0^{\rm des}$), the CO jumps from type-1 sites to regular sites should be faster than those from regular sites to type-1 sites, i.e., $k_{10}^{\rm dif}>k_{01}^{\rm dif}$. The MC probabilities for CO adsorption, desorption, and diffusion jumps are proportional to the corre-

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sponding rate constants and accordingly should also satisfy the conditions above. In the HM simulations, this is however not the case.

In real systems, CO diffusion is fast compared to other steps (see the discussion below). In this case, the relative coverages of regular and defect sites depend primarily on CO diffusion. As already mentioned, HM assume that the probabilities of CO jumps between different sites are equal and accordingly under the steady-state conditions their algorithm should result in nearly equal CO coverages of different sites. A correct MC algorithm should however predict the ratio of CO coverages which is close to that given by the grand canonical distribution. For example, the CO coverages of regular and type-1 defect sites θ_0 and θ_1 have to be related as (to reduce the size of the equation, we neglect here oxygen and type-2 defects)

$$\frac{k_0^{\mathrm{des}}\theta_0}{1-\theta_0}=\frac{k_1^{\mathrm{des}}\theta_1}{1-\theta_1}. \tag{3}$$

This relationship, directly connected with Eq. (2), indicates that in the case studied by HM (when $k_1^{\mathrm{des}} \gg k_0^{\mathrm{des}}$) the correctly calculated CO coverage of type-1 defect sites has often to be much lower than that of regular sites. Thus, the HM algorithm may overestimate the CO coverage of type-1 defect sites and accordingly overestimate the contribution of these sites to the total rate of CO desorption. The influence of type-1 defect sites on the bistability diagram may be overestimated as well.

(2) Referring to real systems, HM declare that they try to simulate the kinetics of CO oxidation with rapid CO diffusion. Despite this declaration, they however assume that the reaction between CO and O species adsorbed in nn sites occurs immediately. Physically, this means that the CO+O reaction is fast compared to CO diffusion, i.e., this reaction is basically limited by CO diffusion. This seems to be a reason why the HM simulations executed for rapid CO diffusion indicate that ''the width of the hysteresis loop decreases with the decrease of the diffusion rate.'' In reality, however, CO diffusion is much faster than the CO+O step. On Pt(111), for example, the experiment and density functional theory (DFT) calculations [7,8] indicate that the activation energy for the CO+O reaction is between 70 and 100 kJ/mol. In contrast, the activation barrier for CO diffusion is lower or about 40 kJ/mol [9]. The preexponential factors for these processes are comparable. Thus, the CO+O step is not limited by CO diffusion. (Note that in abstract MC simulations, motivated by experimental studies of CO oxidation, the Arrhenius parameters for reaction steps and adsorbate diffusion are usually not discussed, CO diffusion is often ignored, or the reaction is postulated to be limited by CO diffusion. Sometimes, e.g., in Ref. [10], the Arrhenius parameters for reaction steps are presented, but the corresponding parameters for CO diffusion are not mentioned. To validate their model, HM might refer to such simulations, but this reference would be irrelevant.)

The incorrect ratio (compared to reality) of the rates of the CO+O reaction and CO diffusion may result in artificial segregation of CO and O species and also in wrong conclusions on the role of CO diffusion in bistability. In particular, contrary to the HM predictions, the hysteresis loop in real systems is not expected to be too sensitive to the rate of CO diffusion provided that this rate is sufficiently high.

Finally, it is appropriate to note that for a particular set of the model parameters (e.g., in Fig. 2(a) of Ref. [6]) the role of the factors discussed above may or may not be quantitatively significant. Anyway, however, the comments above should be taken into account in order to form a firm basis for MC simulations aimed at the understanding of the role of defect sites in bistable kinetics of CO oxidation on single-crystal surfaces.

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