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

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We do not agree with the Comment of Zhdanov about our recent paper [Phys. Rev. E **66**, 066103 (2002)]. It is not necessary for the system to obey the detailed balance in our paper which is far from the equilibrium state, and some experimental results have shown that the chemisorbed CO molecule has almost unit probability of reacting to produce CO_2 under suitable conditions.

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In our recent paper [1], according to the experimental phenomena by Berdau *et al.* [2], we proposed two kinds of theoretical defects to understand the effect of the inhomogeneities of the catalyst surface on the hysteresis behavior in the CO oxidation system. The desorption of CO is very slow and its difference on different sites may play an important role during the jump from low reactivity to high reactivity. Meanwhile, the adsorption of O_2 is also sensitive to the surface feature. However, the adsorption and diffusion of CO are very rapid, and a little of their differences on the surface just have a trivial effect.

It is well known that the inhomogeneities of the catalyst surface may have an effect on all kinds of processes in surface in various subtle ways, in which many mesoscopic details are not well known until now. In this case, it is very difficult to include all details of the catalyst process in a model and it is suitable to cut off some details as Zhdanov himself has stated in Ref. [3], "Critical phenomenon occurring in adsorbed over-layers at conditions far from equilibrium are of high current interest. To simulate such phenomena, one inevitably needs to employ a series of assumptions and simplification, which should of course reflect the main properties of a system under consideration." Therefore, on the defects, only the differences of the desorption of CO and adsorption of O_2 are taken into account in our model and the effects of the adsorption and diffusion of CO can be neglected. Most importantly, our simulation results are generally in agreement with the experimental phenomena and some details are reexhibited in our model [2].

In the Comment of Zhdanov, the author says that the neglect of the influence of the defects on the CO diffusion contradicts the detailed balance principle and it may overestimate the influence of the defect sites. We do not agree with this viewpoint. First, it is well known that the detailed balance is valid only for the system in the equilibrium state and it is just for a pair of reversible processes. However, it is not necessary for the system to obey the detailed balance in our paper which is far from the equilibrium state, while as a local approximation, the detailed balance is employed to describe the surface diffusion process in nonequilibrium systems in some references, e.g., Ref. [4]. Moreover, Eq. (1) in the Comment is physically unreasonable. It is obvious that the diffusion process of the adsorbed CO on the surface is different from a combination of a desorption of the adsorbate on one site and an adsorption on its nearest-neighbor (nn) vacant site. On one hand, the necessary energy of the jump between the nn sites on the surface in the CO diffusion process is much lower than that of the desorption process, otherwise the CO diffusion will be very slow; on the other hand, during the diffusion process, the diffusion particle is adsorbed on the surface and the CO desorption into the gas phase does not occur.

In reality, an adsorbate CO particle on the surface is subject to different interactions on the surface. For example, Kuzovkov *et al.* [5] thought that the diffusion is mainly governed by the strength of the interaction parallel to the surface, but the adsorption and desorption are controlled by the strength of the interaction perpendicular to the surface.

Second, in our paper [1], the influence of the type-I defects in the model leads to the decrease of the occupied probability of CO on these defect sites to provide enough vacant sites for O_2 adsorption. If the effect of type-I defects on the CO diffusion, is included, the probability of the CO diffusion from type-I defects to regular sites is higher than that from regular sites to type-1 defects because the binding energy of the adsorbed CO on the type-1 defects is lower than that on the unperturbed sites. As a result, the adsorbed CO molecules mainly occupy the regular sites and type-I defects can become a vacant site more easily compared to the regular sites, and then the inhomogeneities of the catalyst surface can have a more important influence on the dynamical process compared to the simulation results in our paper. Therefore in our previous work [1], the influence of type-I defects cannot be overestimated, on the contrary, it is underestimated for the influence of the inhomogeneities of the surface.

With respect to the second point of the Comment, the author criticizes that the ratio of the rates of CO diffusion and reaction between adsorbed CO and O species is opposite compared to that observed in reality. However, this is not true. Actually, Sholl and Skodje [6] have reviewed the relationship between the diffusion rate of the adsorbate CO and reaction rate of CO+O, in which it is shown that many factors can have an important effect on the reaction and diffusion rates, such as the reaction temperature, the surface condition, and adsorbed species [6], and that the rates of diffusion and reaction can change in a large range under different conditions. On the other hand, in previous works

[7–12], it is widely accepted that the reaction rate of CO+O species adsorbed in nn sites on surface can be assumed to be infinite. In fact, some experimental results have shown that the chemisorbed CO molecule has almost unit probability of reacting to produce CO_2 under suitable conditions [13]. Therefore, as a theoretical model, we think that our assumption that adsorbed CO can react with adsorbed O on the nn sites with one unit probability, is suitable.

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