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A Model for the CO Oxidation Reaction over a Catalyst Surface with Microscopic Nonuniformities

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Abstract—A modified lattice gas model for heterogeneous CO oxidation is proposed that takes into account microscopic nonuniformities of the catalyst surface. It is shown that, in contrast to the conventional model that assumes that the surface is uniform, according to the modified model the surface is not poisoned with the O_2 phase when the concentration of nonuniformities is high. The mechanism considered in this paper may partly explain the behavior of the reaction system in the region of low CO concentrations.

INTRODUCTION

CO oxidation on platinum group metal surfaces is an important commercial process and a classical model for studying catalytic reactions in the adsorbed layer. The kinetics of this process is determined by the Langmuir–Hinshelwood mechanism:

$$CO_{(g)} + (*) \longrightarrow CO_{(ads)}, \qquad \text{(I)}$$

$$O_{2(g)} + 2(*) \longrightarrow 2O_{(ads)}, \qquad \text{(II)}$$

$$CO_{(ads)} + O_{(ads)} \longrightarrow CO_{2(g)} + 2(*), \qquad \text{(III)}$$

where (*) is a free site on a surface, and subscripts (g) and (ads) refer to the gaseous and adsorbed states respectively.

The numeric description of such reactions has been proposed by Ziff, Gulari, and Barshad [1] (the so-called ZGB model). On an infinite two-dimensional lattice in the time regime $t \longrightarrow \infty$, the behavior of the reaction system is only determined by a ratio of the partial pressures of reactants in the gas phase ($Y_{O_2, CO} = P_{O_2, CO}/(P_{O_2} + P_{CO})$). Because the equality $Y_{O_2} + Y_{CO} = 1$ is fulfilled, the model contains only one independent parameter, which is the molar concentration of CO (Y_{CO}) in the gas phase. Depending on the value of this parameter, the model predicts the existence of three steady states in the reaction, which are shown in Fig. 1: the inactive state of the surface poisoned with oxygen at $Y_{CO} < Y_1$, the inactive state of the surface poisoned with carbon dioxide at $Y_{CO} > Y_2$, and the steady state of the reaction at $Y_1 < Y_{CO} < Y_2$. A change in the state of the system when one passes from one steady-state region to another corresponds to the first-order (Y_2) or second-order (Y_1) phase transition. The range of concentrations $Y_1 < Y_{CO} < Y_2$ where the steady state reaction may occur is referred to as the reactivity zone. The phase transition associated with catalyst poisoning with CO at $Y_{CO} = Y_2$ has been confirmed in experiments, whereas there is no evidence of the catalyst poisoning by oxygen [2]. Modifications of the ZGB model has been proposed to bring it to conformity with experiment.

The extended versions of the model reviewed in [3] take into account the role of spontaneous CO desorption and diffusion along the surface, lateral interactions, the possibility of the Eley–Rideal mechanism, and the modified mechanisms of adsorption. Recently, considerable attention has been given to the properties of a surface: the effect of a subsurface layer [4], the fractal

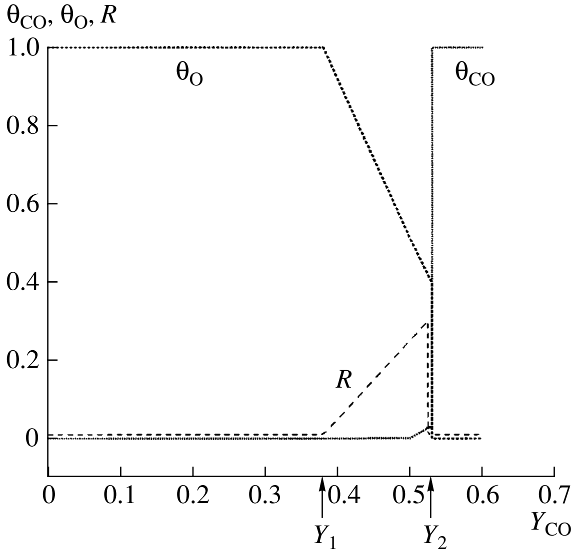

Fig. 1. Dependence of the reaction rate R on the catalyst surface coverage with the phases of CO and O (θ_{CO} and θ_O, respectively) on the molar fraction of CO in the gas phase Y_{CO} in the conventional ZGB model [1]. Y_1 and Y_2 are the critical points in the reaction system corresponding to the second- and first-order phase transitions, respectively.

nature of the surface [3, 5], surface reconstruction [6], surface sites with various coordination [7] and energetics [8]. It was shown that, in the generalized models, the position of critical points Y_1 and Y_2 changes. Some of the mechanisms considered in the literature affect the second-order transition at Y_1. We propose a new version of the model that assumes microscopic nonuniformities of a surface (which can be due to impurities, dislocations, and other factors).

MODEL

In this work we consider a modified ZGB model, which differs from the initial version [1] in the rules of adsorption and reactant interaction. As in the initial variant, we used the Monte Carlo method for modeling. The metal surface was modeled by a regular 128×128 square (with coordination number $Z = 4$) or triangular ($Z = 6$) lattice with periodic boundary conditions. We introduced “broken” site–site bonds to model the presence of microscopic nonuniformities. Broken bonds are distributed over the lattice at random: without correlations in the case of dislocations and with correlations in the case of contaminants or missing surface atoms. The number of broken bonds was a variable parameter.

Lattice sites were the adsorption sites for the surface. A CO molecule requires one site, and an O_2 molecule requires two sites with a nonbroken bond between them. The molecule for adsorption (CO or O_2) is randomly chosen at each step with a probability proportional to the molar fraction of the molecule in the gas phase. Oxygen adsorption is accompanied by its immediate dissociation (II). If CO and O are at the neighboring sites, they enter reaction (III) and the respective sites are freed. The model assumes that all sites are equal in their reactivities.

We consider two variants of the model. According to the first variant (model I), broken bonds prevent both O_2 adsorption and CO + O reaction. The other model (model II) assumes that broken bonds prevent O_2 adsorption, but allow CO + O reaction. The reaction rate is defined as the average number of reacted pairs per iteration (adsorption attempt). Iterations are repeated many times until equilibrium is reached when the fraction of sites occupied by CO and O phases and the average number of reacted pairs stop changing from one iteration to another (at this state there is no dependence on time).

DISCUSSION

Our main observations are as follows. As the number of broken bonds is increased, the critical point Y_1 monotonically shifts toward lower CO concentrations. When the fraction of broken bonds is rather high (~25%), the transition associated with catalyst surface poisoning by O_2 disappears and the zone of a steady-state reaction begins from any low value of Y_{CO}. Numeric data are shown in Figs. 2–4. Figure 2 shows a change in the surface coverage with CO and O phases on square and triangular lattices depending on Y_{CO}. In either case, the catalyst surface is not poisoned by O_2 because of the presence of broken bonds, which according to the model assumption prevent dimer adsorption and do not affect CO adsorption. The effect of broken bonds on O_2 adsorption is seen in the case of the square lattice better than in the case of the triangular lattice because when the fraction of broken bonds is the same for both lattices the overall number of nonbroken bonds is higher in the case of a triangular lattice (Figs. 2, 3, curves *1*, *3*). The triangular lattice has more sites for O_2 adsorption than the square lattice, and the surface coverage with O_2 is higher at all values of Y_{CO}.

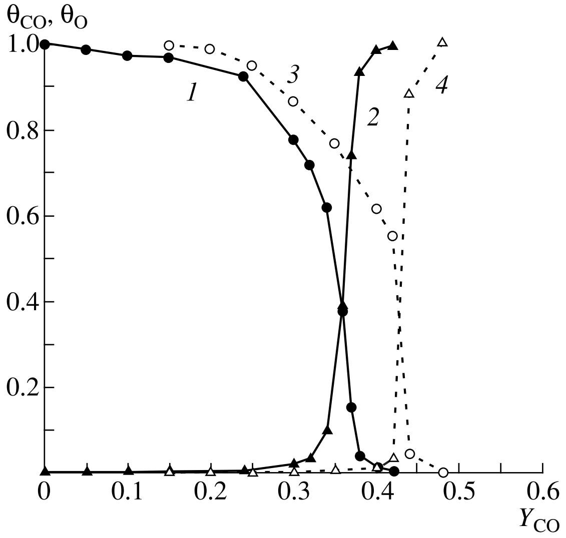

Fig. 2. Dependences of the catalyst surface coverage with CO and O on the CO molar fraction in modified model II for the number of broken bonds equal to ~25%. Square lattice: (*1*) O, (*2*) CO; triangular lattice: (*3*) O, (*4*) CO.

Hindered O_2 adsorption in the region of low Y_{CO} values creates favorable conditions for the adsorption of deficient CO monomers and for the occurrence of the surface reaction. For the reasons explained above, in the region of low Y_{CO} concentrations, the rate of reaction on the square lattice is higher than on the triangular lattice (Fig. 3, curves *2*, *3*). At higher values of Y_{CO}, when none of the phases is deficient, the triangular lattice shows a higher rate because its coordination number is higher and because there are more options for pairwise interactions. The much lower reactivity of the system in model I reflects the additional constraint on the interaction via a broken bond (Fig. 3, curve *1*). Note that the mechanism considered above can only partly explain the reaction behavior at low CO concentrations because the dependence of the reaction rate on Y_{CO} in both models is nonlinear, unlike in the experiment [2].

Finally, in the region of high Y_{CO} concentrations, where the O_2 phase is deficient, the constraint on O_2 adsorption on broken bonds favors surface poisoning with the CO phase. As a consequence, the reactivity

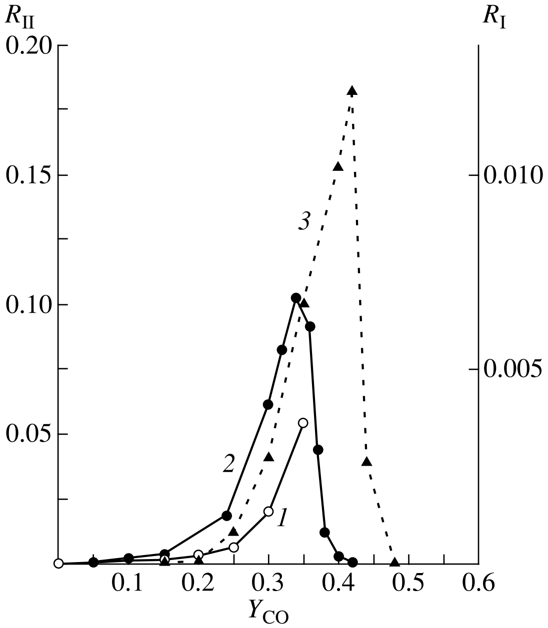

Fig. 3. Dependence of the reaction rate on the molar fraction of CO in model I (curve *1*) and II (curve *2*) on the square lattice and in model II on the triangular lattice (curve *3*). Results for model I are magnified 15 times and only the initial portion of the curve is presented.

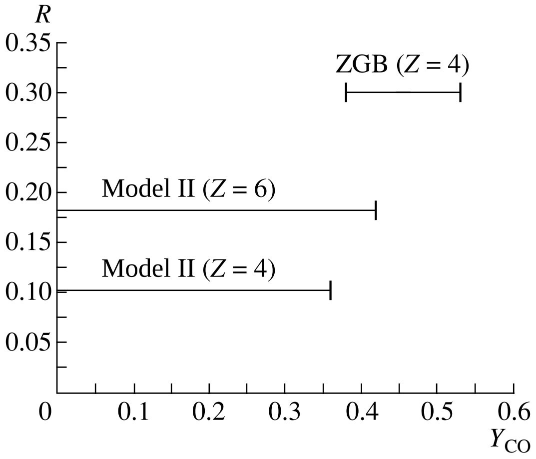

Fig. 4. The reactivity zone in model II on the triangular and square lattices and in the conventional ZGB model. The boundaries of segments correspond to the maximal rate achieved in the reaction.

zone shifts toward lower Y_{CO} values compared with the conventional ZGB model (Fig. 4).

On the triangular lattice, the reaction occurs at a higher rate and in a broader range of concentrations than on the square lattice. This fact agrees with the results of modeling reported in [9]. This is probably due to the higher coordination number of the triangular lattice. Experimental measurements also show that the reaction is structure sensitive [2], however, the role of the surface is not limited to the dependence on the coordination number, because the probability of oxygen adsorption is sensitive to other factors as well.

In conclusion, we would like to note that the mechanism proposed here for the effect of microscopic nonuniformities of the surface is similar to that reported in [5] where the catalytically active surface consisted of an infinitely great number of fractal clusters. In both cases (because of the deterioration of adsorption sites in our model and because of the existence of clusters with an odd number of sites in the model proposed in [5]), complete coverage of the surface with dimer molecules is impossible. Free sites play the role of adsorption sites for monomeric molecules and work as reaction sites.

The effect of surface nonuniformities has also been studied by Cortes and Valencia [10], but their description was different. Nonuniformities had the form of strips or terraces, which were infinite in one dimension and bounded in other directions. Despite the difference between the model proposed in [10] and our model, conclusions are qualitatively similar: surface poisoning by oxygen becomes impossible only if the concentration of nonuniformities is sufficiently high (~25% according to [10] as well), and the dependence of the reaction rate on the molar fraction of CO in the region of low Y_{CO} values remains nonlinear.

CONCLUSIONS

As the fraction of broken bonds increases, the boundaries of the reactivity zone monotonically shift toward lower CO concentrations. When the fraction of broken bonds is ~25%, the phase transition associated with the poisoning by oxygen disappears and the reaction begins at Y_{CO}. This effect is more pronounced and the reaction rate is higher in the case of model II when broken bonds prevent O_2 adsorption but allow the reaction. The mechanism considered here can explain in part the behavior of the reaction system in the range of low CO concentrations.

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