

# Modeling of Surface CO Oxidation Using Modified Adsorption Rules

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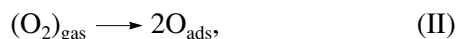
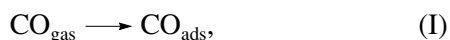
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**Abstract**—Lattice models based on modified adsorption and interaction rules are suggested for heterogeneous CO oxidation. The advantage of these models over the conventional model is that they disavow the false prediction that the catalytic surface will be poisoned by oxygen at low CO concentrations in the reaction mixture. In the general case, the way the reaction rate and CO and O coverages vary with CO concentration is sensitive to the choice of adsorption rules.

Carbon monoxide oxidation on platinum metals is a classical model of surface processes. A numerical model of this reaction was suggested by Ziff, Gulari, and Barshad [1] (ZGB model). This model is based on the Langmuir–Hinshelwood mechanism and includes the following steps:



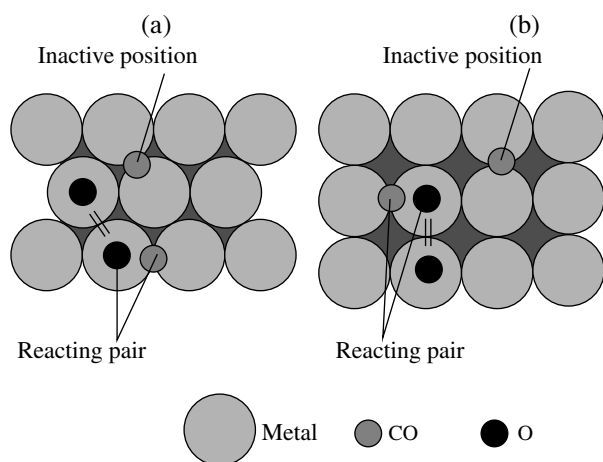
The behavior of this model system on an infinite two-dimensional surface at an infinite time ( $t \rightarrow \infty$ ) is determined only by the ratio of the partial pressures of the reactants in the gas phase,  $Y_{\text{CO}, \text{O}_2} = P_{\text{CO}, \text{O}_2} / (P_{\text{CO}} + P_{\text{O}_2})$ . Since  $Y_{\text{CO}} + Y_{\text{O}_2} = 1$ , the model has a single independent numerical parameter, specifically, the molar fraction of carbon monoxide in the gas phase  $Y_{\text{CO}}$ . The properties of the ZGB model and its modifications are detailed elsewhere [2–11].

A drawback of this model is that it predicts poisoning of the surface by adsorbed oxygen at small CO concentrations in the gas phase. In fact, this poisoning has never been observed [12, 13]. Earlier, we considered the effect of surface microinhomogeneities on the reaction and demonstrated that, when the microinhomogeneity concentration is rather high (~25%), the surface is not poisoned by oxygen [14]. However, this effect can only partially be responsible for the behavior of the system.

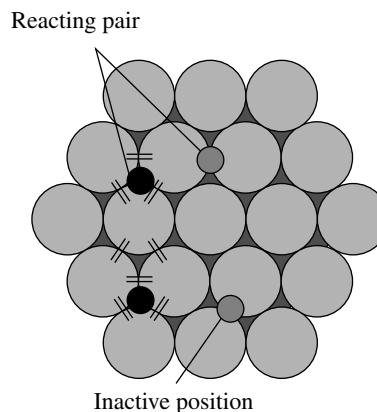
In this publication, we suggest a new version of the model. We assume that different phases occupy different types of adsorption sites and that there are different types of adsorption.

## MODELS

Here, we consider two models that differ from the original ZGB model [1] in reactant adsorption and interaction rules. As in the original version, modeling is carried out by the Monte Carlo method. The metal surface is viewed as a regular square lattice with a coordination number of  $Z = 4$  or a triangular lattice with  $Z = 6$ . The lattice has  $128 \times 128$  nodes and the corresponding number of bonds. Periodical boundary conditions are imposed to obviate effects due to lattice finiteness. The sequence of operations making up one Monte Carlo iteration is as follows. First, an adsorbed molecule ( $\text{CO}$  or  $\text{O}_2$ ) is chosen at random with probability proportional to its mole fraction in the gas phase. Next, a hypothetical adsorption site is chosen at random. Conditions under which adsorption is considered possible depend on the model chosen and are described below. If adsorption at a given site is impossible, the iteration is terminated. Upon successful adsorption, an  $\text{O}_2$  molecule dissociates immediately by reaction (II). If  $\text{CO}$  and  $\text{O}$  are adsorbed at neighboring sites, they react according to reaction (III) to vacate both of the sites. At this point, the iteration is finished. The reaction rate is conditionally defined as the mean number of reacted pairs per iteration (an adsorption attempt). These iterations are repeated many times until the sys-



**Fig. 1.** Arrangement of adsorbates on the metal surface in the bridging CO model with (a) a triangular and (b) a square lattice. The symbol = marks the bonds that must be vacant for an oxygen molecule to be adsorbed.



**Fig. 2.** Arrangement of the adsorbates on the metal surface in the interstitial oxygen model for the [111] crystal face.

tem comes to equilibrium, which is the state in which the number of adsorption sites occupied by CO and O and the number of reacted pairs no longer change from one iteration to another (are time-independent).

First, we present the *bridging CO model*, in which lattice bonds serve as adsorption sites for CO molecules.<sup>1</sup> One unoccupied bond is necessary for adsorption of a CO molecule. One O<sub>2</sub> molecule needs two neighboring nodes and a vacant bond between them (Fig. 1). Adsorbed CO and O can react only when they share a lattice node.

The second model is called the *hollow-site oxygen model*. Here, as in the previous model, adsorption sites for CO molecules are lattice bonds. However, the following steric constraint is imposed: any lattice node may be involved in adsorption of at most one CO molecule. The maximum CO coverage of the surface is 1/2 of the monolayer. Adsorption sites for O atoms are hollows (Fig. 2), and any lattice node may be involved in adsorption of at most one O atom. Accordingly, the maximum O coverage of the surface is 1/3 of the monolayer. (Only a triangular lattice was considered in this case.) The above steric constraints are consistent with the conventional notion of oxygen and carbon monoxide adsorption on the (111) face of platinum metal crystals [15]. For O<sub>2</sub> adsorption in the presence of CO, it is also necessary that the bonds labeled “=” in Fig. 2 be vacant. The three bonds around a hollow site occupied

by an adsorbed O atom are considered to be unavailable for CO. As in the first model, adsorbed CO and O can react only when they share a common lattice node.

## RESULTS AND DISCUSSION

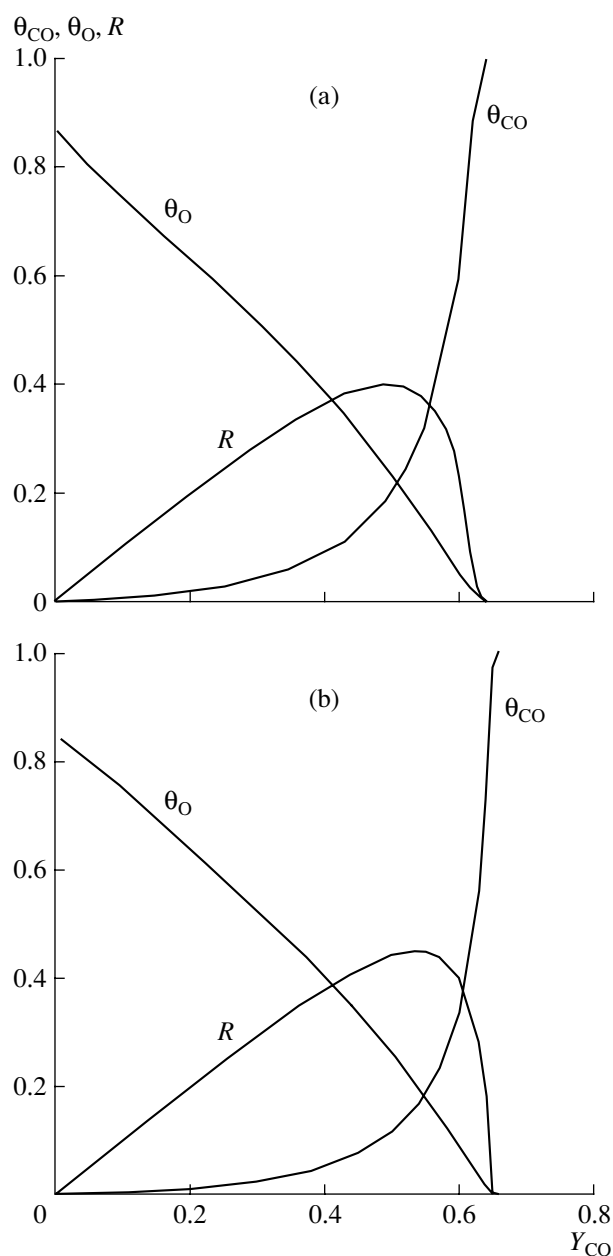
### *Bridging CO Model*

The results obtained with square and triangular lattices are presented in Figs. 3a and 3b, respectively. When CO molar fractions ( $Y_{\text{CO}}$ ) are low, the reactants do not compete for adsorption sites; therefore, there can be no poisoning of the surface by the O phase and the reaction rate  $R$  changes linearly with  $Y_{\text{CO}}$ . Note that the O coverage of the surface at  $Y_{\text{CO}} = 0$  is always below unity, because random O<sub>2</sub> adsorption cannot result in dense packing. At high CO concentrations, steric constraints come into play to prevent O<sub>2</sub> adsorption. After a well-defined maximum, the reaction rate falls rapidly to zero and the coverages  $\theta_{\text{CO}}$  and  $\theta_{\text{O}}$  tend to 1 and 0, respectively. The abrupt change in the slope of all curves in Fig. 3 indicates a first-order phase transition. This behavior is deduced for both triangular and square lattices and is in qualitative agreement with experimental data [12]. The comparative simplicity of this model makes it useful in phenomenological applications.

### *Hollow-Site Oxygen Model*

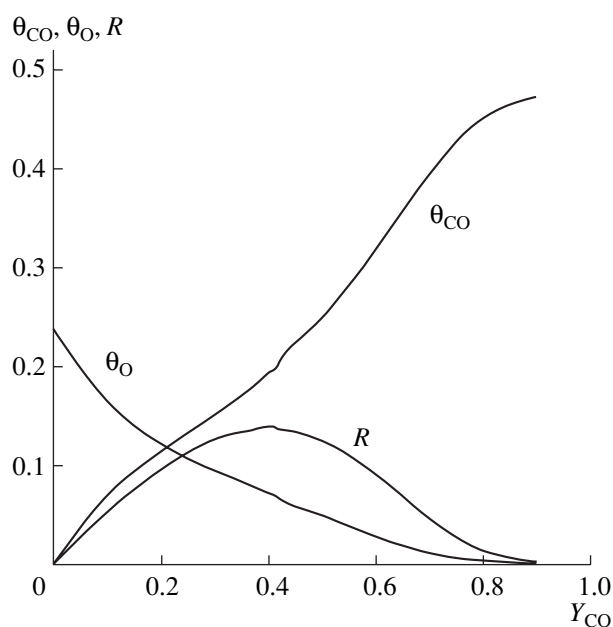
Main results obtained with this model are presented in Fig. 4. The competition between the reactants is retained but it is rather weak at low CO concentrations. As a consequence, the surface is not poisoned by the O phase, as in the previous model. Because of the much

<sup>1</sup> Hereafter, we use the term *lattice bond* in a mathematical, not chemical, sense.



**Fig. 3.** Reaction rate ( $R$ ) and CO and O coverages of the surface ( $\theta_{\text{CO}}$  and  $\theta_{\text{O}}$ ) as a function of the mole fraction of CO in the gas phase ( $Y_{\text{CO}}$ ) for the bridging CO model with (a) a square and (b) a triangular lattice.

more severe steric constraints, both the CO and O<sub>2</sub> coverages of the surface are markedly lower at any  $Y_{\text{CO}}$ . It is most likely that the much smaller slope of the  $R(Y_{\text{CO}})$  curve is also due to the steric constraints. The inference that the surface is not poisoned by oxygen at small  $Y_{\text{CO}}$  values is in agreement with experimental data [12]. However, a gradual decrease in the reaction rate at high  $Y_{\text{CO}}$  values, which indicates no phase transition, conflicts with experimental data.



**Fig. 4.** A plot of the reaction rate ( $R$ ) and CO and O coverages of the surface ( $\theta_{\text{CO}}$  and  $\theta_{\text{O}}$ ) vs. the molar fraction of CO in the gas phase ( $Y_{\text{CO}}$ ) in the hollow-site oxygen model for the (111) crystal face.

## CONCLUSION

Obviously, the behavior of a model system within the same kinetic mechanism depends crucially on the adsorption rules and steric constraints. In particular, the assumption that different reactants are adsorbed on different types of sites and, therefore, compete only softly leads to the inference that there is no phase transition due to surface poisoning by CO.

At first glance, the hollow-site oxygen model includes more realistic adsorption rules and steric constraints than the bridging CO model. However, it is in poorer agreement with experimental data. Therefore, even a model with quite realistic adsorption rules may be invalid. To correctly describe a phenomenon on a quantitative (or even qualitative) level, it is necessary to take into consideration other physical processes. The most significant of these is diffusion, which plays the most important role in reactant distribution over the surface. Now we are developing a more complete model of the reaction.

## REFERENCES

1. Ziff, R.M., Gulari, E., and Barshad, Y., *Phys. Rev. Lett.*, 1986, vol. 56, no. 3, p. 2553.
2. Albano, E.V., *Heterog. Chem. Rev.*, 1996, vol. 3, p. 389.
3. Head, D.A. and Rodgers, G.J., *Phys. Rev. E*, 1996, vol. 54, no. 2, p. 1101.
4. Park, H., Kim, H., and Lee, S., *Surf. Sci.*, 1997, vol. 380, nos. 2–3, p. 514.

5. Albano, E.V., *Langmuir*, 1997, vol. 13, p. 4013.
6. Cortes, J. and Valencia, E., *Surf. Sci.*, 1997, vol. 371, no. 1, p. L243.
7. Meakin, P. and Scalapino, D.J., *J. Chem. Phys.*, 1987, vol. 87, no. 1, p. 731.
8. Bagnoli, F., Sente, B., Dumont, M., and Dagonnier, R., *J. Chem. Phys.*, 1991, vol. 94, no. 1, p. 777.
9. Tammaro, M. and Evans, J.W., *Phys. Rev. E*, 1995, vol. 52, no. 3A, p. 2310.
10. Cortes, J. and Valencia, E., *Surf. Sci.*, 1999, vol. 425, no. 1, p. L357.
11. Khan, K.M. and Ahmed, N., *Physica A*, 2000, vol. 280, nos. 3–4, p. 391.
12. Ehsasi, M., Matloch, M., Frank, O., *et al.*, *J. Chem. Phys.*, 1989, vol. 91, no. 8, p. 4949.
13. Dumont, M., Dufour, P., Sente, B., and Dagonnier, R., *J. Catal.*, 1990, vol. 122, no. 1, p. 95.
14. Abramova, L.A., Baranov, S.P., and Dulov, A.A., *Kinet. Katal.*, 2003, vol. 44, no. 5, p. 1.
15. Boreskov, G.K., in *Catalysis: Science and Technology*, 1982, vol. 3, p. 40.