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Computer simulations studies of the catalytic oxidation of carbon monoxide on platinum metals

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Computer simulations studies of the catalytic oxidation of carbon monoxide on platinum metals

H.-P. Kaukonen and R. M. Nieminen

Laboratory of Physics, Helsinki University of Technology, SF-02150 Espoo, Finland

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The steady-state catalytic oxidation process of carbon monoxide on platinum metal surfaces is studied using two irreversible kinetic computer simulation models: (a) An extended version of the model introduced by Ziff, Gulari, and Barshad (ZGB) with the effects of CO desorption and diffusion as well as finite reaction probability taken into account. The different physical processes, diffusion and desorption are studied independently and their effect on the equilibrium window, i.e., the regime where steady CO₂ formation occurs is determined. (b) An interaction model where adatom–adatom nearest-neighbor (nn) interactions are taken explicitly into account through Boltzmann terms J_1 , J_2 , and J_3 which are the energies of the CO–CO, O–O, and CO–O interactions, respectively. The phase diagrams in the temperature–CO-partial pressure (T, p_{CO}) plane are determined for different values of the nn interactions. The behavior of the system is dependent on the sign of J_1 ($= J_2$ in the simulations) as well as the sign of the difference $J_1 - J_3$. There is thus a clear analogy with a two-component equilibrium lattice gas with nn interactions.

I. INTRODUCTION

The catalytic oxidation reaction

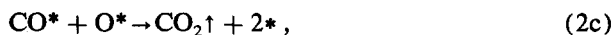


on platinum surfaces has recently been studied at the microscopic level using Monte Carlo (MC)-related computer simulations. The purpose of these studies has been to investigate the effects of the local structure of the adlayer and adatom–adatom interactions on the rates of the elementary reaction steps, adsorption, diffusion, surface reaction, and desorption, and thereby on the overall reaction rate. The results indicate that cluster formation causes the reaction rate to differ significantly from that obtained from classical Langmuir–Hinshelwood kinetics, where molecules are assumed to be randomly distributed on the surface. The effect of interactions between adsorbed molecules can be divided into two classes: (a) topological effects, i.e., the change in nearest-neighbor (nn) distributions which affects reactivity through a change in the frequency of reactive collisions, and (b) bond formation between adatoms, which affects the activation energies of different reaction steps.

The models presented so far have mostly been kinetic. The effect of microscopic structure has been modeled into the kinetic coefficients of the reaction steps instead of taking adatom–adatom interactions explicitly into account. Ben-Shaul and Silverberg^{1,2} have studied the reaction by combining MC methods for the rate determining step and lattice gas methods to calculate the rates of the other elementary steps, taking nn interactions into account through Maxwell–Boltzmann terms. They first adsorbed a coverage θ_A of molecules A on the surface and let them aggregate due to attractive A–A nn interactions for a time period t_d . The diffusion rate of A molecules was assumed to be much slower than that of molecules B. At t_d a coverage θ_B of B molecules are allowed to adsorb on the surface and to react with A molecules when-

ever AB nn pairs are formed and a reaction condition is satisfied. Strong influence of cluster formation was seen. Further adsorption of either molecule was not allowed and therefore their model gives no information of the long-time behavior of the system.

In this work we study the long-time behavior of the catalytic system and the conditions where steady state continuous total reaction rates can be achieved. Our approach is based on the nonequilibrium kinetic model introduced by Ziff, Gulari, and Barshad (ZGB).³ The ZGB model is based on three reaction steps:



where * stands for an empty site/adsorbed molecule. The principle of the model is briefly explained below, a more detailed discussion can be found in Ref. 3. In the ZGB model the catalytic surface is represented by a square lattice of adsorption sites. A CO or O₂ molecule is then selected at random to hit the surface. Oxygen adsorption is assumed to occur dissociatively, both oxygen atoms filling a site. Thus, if the molecule is O₂, two nearest-neighbor sites are chosen from the lattice, whereas CO adsorption requires only one adsorption site. If the randomly chosen site or one of the two nn sites are occupied the adsorbing molecule bounces off the surface and a new molecule and an adsorption site or sites are chosen. Whenever a molecule is adsorbed the local environment, i.e., all nn sites are scanned and all CO–O pairs are removed from the surface, which constitutes the Langmuir–Hinshelwood reaction step. The long-time behavior of the system is characterized by only one parameter, p_{CO} , which describes the selection probability of choosing a CO molecule. ($p_{\text{O}_2} = 1 - p_{\text{CO}}$). Within a critical range, $p_1 < p_{\text{CO}} < p_2$, the “equilibrium window”, the coverage θ_{CO}

and θ_{O} reach a steady nonzero value and CO_2 -production occurs at a constant rate. When $p_{\text{CO}} < p_1$ ($p_{\text{CO}} > p_2$) the surface is rapidly poisoned with oxygen (carbon monoxide). The transition at p_1 is continuous, whereas at p_2 the system has a first-order(like) kinetic phase transition. The ZGB model has also been studied by Meakin and Scalapino⁴ who extended the model to a hexagonal lattice and narrow strips. The qualitative behavior of the model remained the same for the hexagonal lattice and for strips wider than 3 lattice units. For narrower strips an equilibrium window could not be found.

It is clear that while of considerable conceptual interest such a model is a gross oversimplification of the actual catalytic process. A more realistic treatment should consider at least the effects of surface diffusion, desorption, and nn interactions. Recently, Araya *et al.*⁵ have reported a study where they have analyzed the effect on elementary processes of the algorithm chosen to account for nn interactions in MC-related kinetic models. They also performed a comparison with published models. Their results show that the models considered are sensitive to the algorithm chosen to account for nn pairs, which can lead to nonunique behavior changing the location of the equilibrium window. The effect of reducing the reaction probability was to shift the equilibrium window to what would correspond to lower p_{CO} values in the ZGB model. The authors concluded that desorption decreases the average CO cluster size which leads to a better agreement between LH and MC calculations. Surface diffusion was not considered in their model.

In the present work we aim at a more realistic model of the surface reaction (1) and present cellular automaton and MC studies of the steady-state properties. The work is divided into two parts:

(i) In Sec. II we extend the ZGB model by adding surface diffusion, desorption, and finite reaction probability into the model. The qualitative effect of the new parameters on the equilibrium window and the total CO_2 production rate is examined.

(ii) In Sec. III we introduce a new model which takes nn interactions explicitly into account. The local interactions change the probabilities of different elementary steps, which results in interesting behavior as the temperature is lowered.

The conclusions are summarized in Sec. IV.

II. EXTENDED ZGB MODEL

Three new parameters were added to the ZGB model: the CO desorption probability R_d , the CO surface diffusion probability D , and the reaction probability p_r . Diffusion and desorption of oxygen were neglected since measurements on platinum metal surfaces indicate that the surface consists of a mobile CO phase interacting with a practically immobile oxygen phase.⁶ Oxygen desorption and diffusion are not important at typical reaction conditions. The CO molecules were assumed to be independent of each other with respect to these elementary processes. Accordingly, R_d , D , and p_r denote the probabilities/time of single CO molecules to desorb, diffuse to an nn site, and react with a neighboring O atom, respectively. (In the new model discussed in Sec. III below local interactions do change these probabilities.) Dur-

ing each cycle of simulation, i.e., after each adsorption trial, the number of desorbing CO molecules is determined as a random variable n_{des} from a binomial distribution with the expectation value $N_{\text{CO}}R_d$,

$$n_{\text{des}} \sim \text{Bin}(N_{\text{CO}}R_d), \quad (3)$$

where N_{CO} is the total instantaneous number of adsorbed CO molecules. The desorbing particles are then removed randomly from the surface.

The number of "candidates" for diffusion is obtained similarly as

$$n_{\text{diff}} \sim \text{Bin}(N_{\text{CO}}D). \quad (4)$$

The diffusion part of the algorithm consists of the following steps: (i) choose a CO molecule at random, (ii) if there exist empty nn sites, pick one randomly and move the molecule, (iii) go to (i). The same molecule may thus move more than one step. Note that even in the extended model no temperature enters explicitly, only via its effect on the parameters R_d , D , and p_r .

When desorption and diffusion are both completed for the cycle the surface is checked for the existence of CO-O pairs which were removed with a probability $p_r < 1$. The simulations were done on a 200×200 lattice with periodic boundary conditions. Typical simulation lengths were $t = 200$ – 1000 cycles, where one cycle consists of one trial/site on the average (i.e., 40 000 trials and subsequent desorption, diffusion, and reaction steps). We did some extended runs up to 10 000 cycles to ensure the stability of the system. Each parameter R_d , D and p_r was systematically varied while keeping the other two constant (typically zero), thus examining the effect of each physical process independently. Some examples of their combined effect were also studied.

Figure 1 shows the steady-state coverage θ_{CO} , θ_{O} and the production rate P as a function of the fraction p_{CO} of carbon monoxide in the gas phase for three different values of R_d . For comparison, also the case $R_d = 0$ is shown. The characteristic first-order behavior near the transition at $p_{\text{CO}} = p_2$ without desorption ($R_d = 0$) is gradually removed by the introduction of a nonzero probability of desorption. The carbon monoxide coverage also naturally depends on the desorption probability. At the extreme limit, $p_{\text{CO}} = 1.0$, the maximum obtainable CO coverage scales as

$$\theta_{\text{CO,max}} = \frac{1}{1 + NR_d}. \quad (5)$$

The smoothing of the transition around p_2 can be readily understood by considering the changes in the adatom cluster structure and local adsorption.

When $R_d = 0$, the average CO cluster size is an increasing function of p_{CO} . Reaction can take place only at the borders of clusters, whereas sites in the cluster interiors are stable. As the lattice starts to fill up adsorption of O_2 is greatly reduced due to the requirement of two adjacent free adsorption sites. Thus, when the CO cluster size reaches a critical value the lattice is rapidly poisoned by CO: there is an analogy with percolation problems.⁷

When $R_d > 0$, desorption slows down the growth of CO clusters and the effective oxygen sticking coefficient is not as greatly reduced. This leads to a spreading of the transition

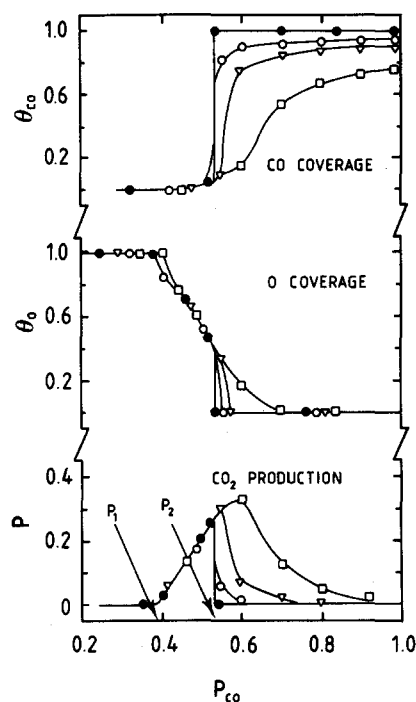


FIG. 1. Surface coverages θ_{CO} , θ_{O} and the production rate P as a function of p_{CO} for four different values of the desorption probability R_d . (●) $R_d = 0$, (○) $R_d = 1.3 \times 10^{-6}$, (▽) $R_d = 2.8 \times 10^{-6}$, and (□) $R_d = 8.3 \times 10^{-6}$. The lattice size $N = 200 \times 200$.

regime. With greater R_d values CO_2 production reaches its maximum rate when the coverages of O and CO are equal, i.e., are in stoichiometric proportion on the surface. This implies a practically random distribution of adsorbed molecules, which leads to the mean-field approximation (MFA) expression for the total rate as $r \sim k\theta_{\text{CO}}\theta_{\text{O}}$, which is maximized, when $\theta_{\text{CO}} = \theta_{\text{O}}$. In general, the MFA rate expression is not valid and the reaction rate depends on the cluster structure of the adsorbed molecules, which has been shown to be the case also for other related kinetic models. The snapshot pictures of Figs. 2(a)–2(c) show the surface in three different cases with the same total CO coverage $\theta_{\text{CO}} \approx 0.40$. Figure 2(a) shows the distribution of CO on the surface when the $N\theta_{\text{CO}}$ sites ($N = 100 \times 100$) are chosen at random. Figure 2(b) is obtained after 2500 simulation cycles when $R_d = 3.32 \times 10^{-5}$ corresponding to $p_{\text{CO}} = 0.65$ (see the squares in Fig. 1). The distribution of CO remains practically uniform. Figure 2(c) shows the surface when $R_d = D = 0$, and $p_{\text{CO}} = 0.535 > p_2$ and θ_{CO} has just reached the value 0.40. The surface would clearly become poisoned by CO (cf. Fig. 1) if the simulation were continued. The comparison of these snapshots supports the conclusion that desorption tends to “randomize” the CO distribution, which leads with increasing desorption to a mean-field reaction rate. To reach optimum steady-state production rates one should try to maximize the coverages of both reactants on the surface. In cases where one coverage is much greater than the other the rate is almost completely determined by the smaller coverage. In most cases θ_{CO} is the critical parameter due to poisoning at p_2 , which effectively

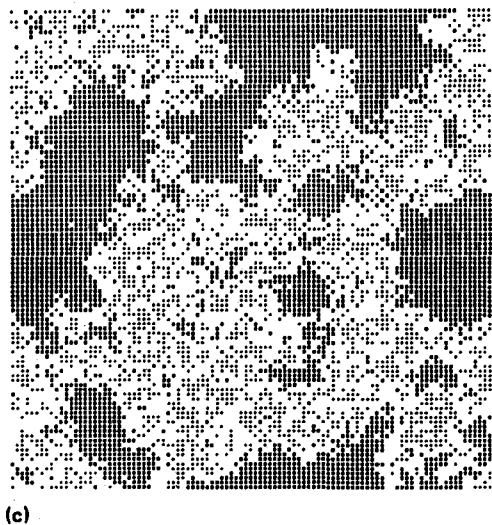
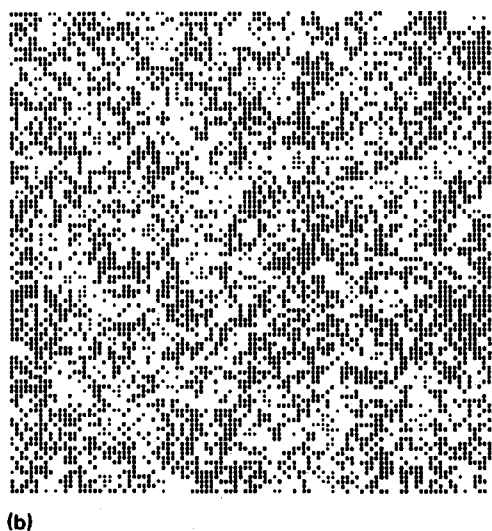
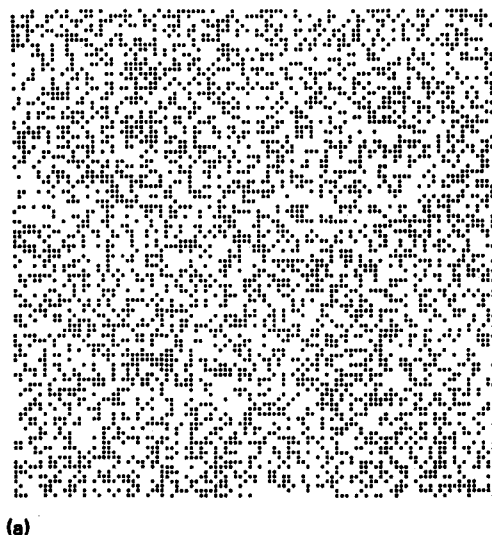


FIG. 2. Snapshot pictures of the surface in different cases with $q_{\text{CO}} \approx 0.40$. (a) A totally random distribution, (b) $R_d = 3.3 \times 10^{-5}$, $p_{\text{CO}} = 0.65$, $t = 2500$ time cycles, and (c) $R_d = D = 0$, $p_{\text{CO}} = 0.535 > p_2$. (+ = O atom, and ■ = CO molecule).

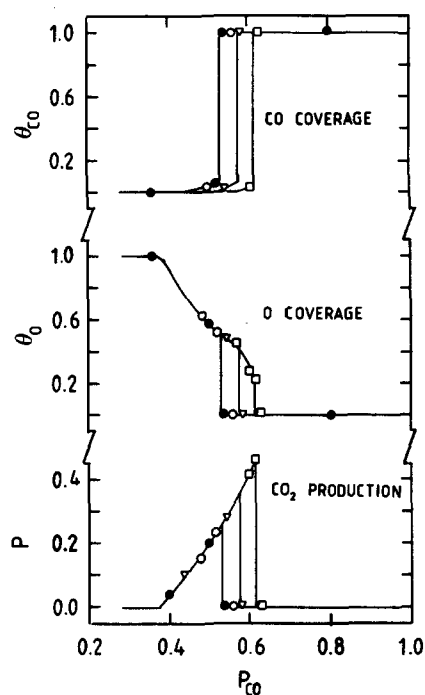


FIG. 3. Surface coverages θ_{CO} , θ_{O} and the production rate P as a function of p_{CO} for four different values of the diffusion probability D . (●) $D=0$, (○) $D=10^{-5}$, (▽) $D=10^{-4}$, and (□) $D=10^{-3}$. The lattice size $N=200 \times 200$.

prevents the formation of large CO coverages on the surface. Due to desorption it is possible to maintain a higher CO coverage on the surface before poisoning. Since the CO coverage is critical for the production rate at lower p_{CO} values, this leads to an increase in the maximum available reaction rate. Also, the control of the system is easier because the system is not as critical with respect to poisoning.

Diffusion can occur only at the boundary sites of CO clusters. The movement of CO molecules increases reactivity and opposes again the growth of CO clusters. This causes a shift in p_2 to higher values. The transition remains first order. As the lattice starts to fill the effective diffusion coefficient $D_{\text{eff}} \rightarrow 0$. Finally a critical cluster size is reached and poisoning into the CO phase occurs as in the case $D=0$. Figure 3 shows the results for three different values of D , as well as for the case $D=0$. The maximum production rate is achieved just at the transition since θ_{CO} is the critical component on the surface.

The combined effect of R_d and D was studied for typical values $R_d = 8.3 \times 10^{-6}$ and $D = 10^{-4}$. ($N = 200 \times 200$). The results are shown in Fig. 4. It is clearly seen that desorption is the dominant parameter, which determines the behavior of the system at p_2 . Diffusion merely sharpens the transition by removing the small remaining oxygen coverage reactively. The maximum reaction rate when both diffusion

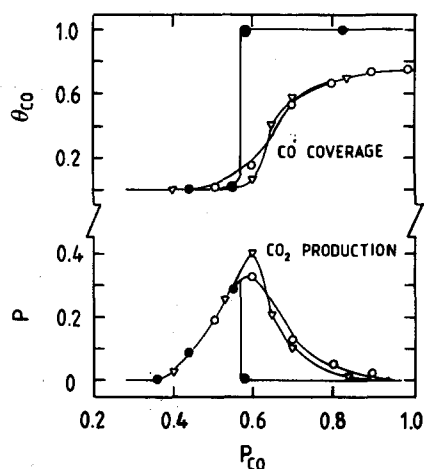


FIG. 4. The combined effect of R_d and D on θ_{CO} and P . (●) $R_d = D = 0$, (○) $R_d = 8.3 \times 10^{-6}$ and $D = 0$, (▽) $R_d = 8.3 \times 10^{-6}$ and $D = 10^{-4}$.

and desorption are present is again greater than in the case when both are absent due to an increase of the maximum steady CO coverage obtainable on the surface.

A detailed study for the finite reaction probability was not performed. The results show, however, a distinct shift of p_2 to the left when p_r is reduced from unity, in agreement with Araya *et al.*⁵ Thus the effect of $p_r < 1$ seems to be similar to that of surface diffusion but to the opposite direction.

III. INTERACTION MODEL

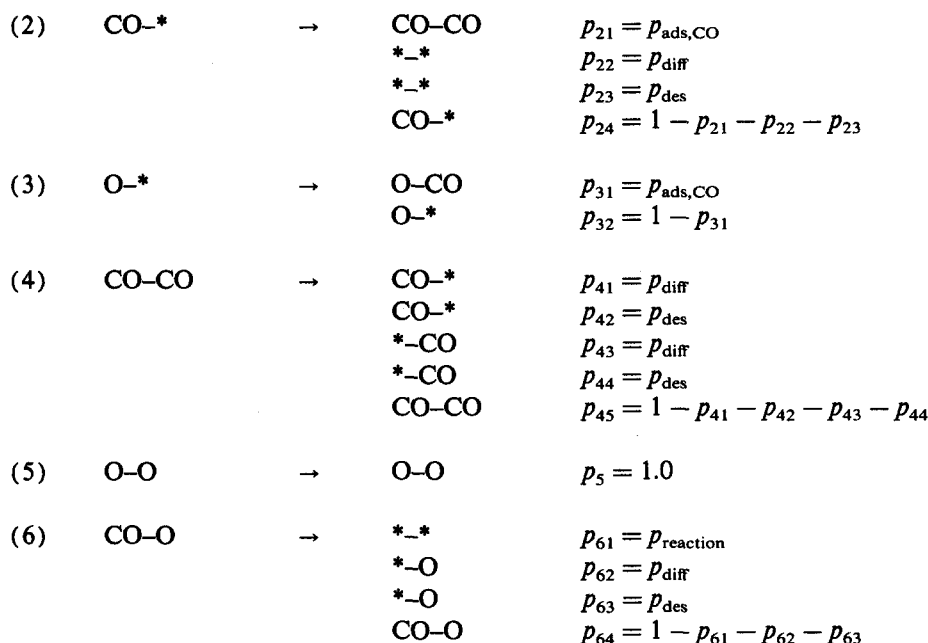
At low temperatures or high coverages the interactions within the adlayer may become important with respect to the reaction rate since they determine the local structure of the surface and the phase diagram in the $T\theta$ plane. We introduce a simple model, which takes into account nearest-neighbor adatom interactions on the surface. The main difference to the extended ZGB model is that we take nn pairs as the basic building blocks of the model. One time cycle corresponds to determining the changes of all the $2N$ nn bonds on the surface in a random order. There are six types of molecule pairs with corresponding energies given below:

	bond	energy
(1)	*-*	0
(2)	CO-*	0
(3)	O-*	0
(4)	CO-CO	J_1
(5)	O-O	J_2
(6)	CO-O	J_3

“*” stands for an empty site.

The evolution of the surface in simulation time is determined by the following set of local rules:

	initial state	→	final state	transition probability
(1)	*-*	→	CO-*	$p_{11} = P_{\text{ads,CO}}$
			*-CO	$p_{12} = P_{\text{ads,CO}}$
			O-O	$p_{13} = P_{\text{ads,O2}}$
			-	$p_{14} = 1 - p_{11} - p_{12} - p_{13}$



The probabilities p_{ij} for the various channels are defined:

$$p_{\text{ads,CO}} = \frac{1}{2} p_{\text{CO}} \min\{1, e^{-\Delta E_1/T}\}, \quad (6a)$$

$$p_{\text{ads,O}_2} = (1 - p_{\text{CO}}) \min\{1, e^{-\Delta E_2/T}\}, \quad (6b)$$

$$p_{\text{des}} = \frac{1}{2} R_d e^{-\Delta E_1/T}, \quad (6c)$$

$$p_{\text{diff}} = \frac{1}{2} D e^{-\Delta E_{\text{diff}}/T}, \quad (6d)$$

$$p_{\text{reaction}} = p_r \min\{1, e^{-\Delta E_r/T}\}, \quad (6e)$$

where

$$\Delta E_1 = E_1(x_1, y_1) - E_0, \quad (7a)$$

$$\Delta E_2 = E_2(x_1, y_1) + E_2(x_2, y_2) + J_2 - E_0, \quad (7b)$$

$$\Delta E_{\text{diff}} = E_1(x_2, y_2) - E_1(x_1, y_1) - J_1, \quad (7c)$$

$$\Delta E_r = E_1(x_1, y_1) + E_2(x_2, y_2) - J_3. \quad (7d)$$

$E_{1,2}(x_i, y_i)$ is the local interaction energy for a molecule ($1 = \text{CO}$, $2 = \text{O}$) if placed in the site (x_i, y_i) , and is simply the sum of all bond energies J_i between the site (x_i, y_i) and its nearest neighbors. E_0 is the reference energy of an empty surface and can be set equal to zero. For example, $p_{\text{ads,CO}}$ consists of three factors. p_{CO} is the probability of choosing a CO molecule. The factor $1/2$ simply accounts for the symmetry of a pair of empty sites. The last factor describes the sticking probability, which is assumed to be 1 for a clean surface. Repulsive nn interactions decrease this probability via a Boltzmann factor dependent on an activation energy. The other terms in Eqs. (6) are obtained in a similar fashion.

The desorption and diffusion coefficients also scale exponentially with temperature:

$$D = D_0^{T_0/T}, \quad (8a)$$

$$R_d = R_{d,0}^{T_0/T}. \quad (8b)$$

T_0 is a reference temperature which can be chosen arbitrarily to fix the energy scale.

If the sum of probabilities of a particular transition (1)–(6) exceeds one, all probabilities are scaled by a normalizing

factor in order to preserve the branching ratios of different processes.

There is a correspondence between the interaction model and the extended ZGB model by defining (unknown) effective parameters $R_{d,\text{eff}}$, D_{eff} , and $p_{r,\text{eff}}$. Figure 5 shows the results when $R_d = D = J_i = 0$ and $p_r = 1.0$. In this limit the model behaves similarly to the original ZGB model except that the equilibrium window is shifted to lower values. This can be understood by the existence of nonreacting CO–O pairs on the surface, which corresponds to an effective lowering of the reaction probability, and the relative weakening of O_2 adsorption. The main features of the model are preserved.

The maximum coverage at $p_{\text{CO}} = 1.0$ follows a similar relation to Eq. (5),

$$\theta_{\text{CO,max}} = \frac{1}{1 + R_d}. \quad (9)$$

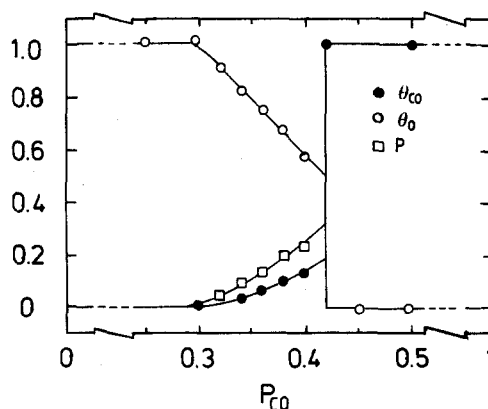


FIG. 5. Surface coverages θ_{CO} , θ_{O} and the production rate P as a function of p_{CO} for the interaction model, when $R_d = D = J_i = 0$, $p_r = 1.0$.

For the subsequent simulations the value of $R_d = 0.1$ was chosen for the desorption probability. This corresponds to $R_d = 2.5 \times 10^{-6}$ in the ZGB model ($N = 200 \times 200$). For the diffusion coefficient a value of $D = 0.1$ was chosen arbitrarily. The simulations were performed on a 100×100 lattice with periodic boundary conditions. In all the simulations we set $J_1 = J_2 \neq J_3$. Different behavior of the system was seen depending on the signs and magnitudes of the adatom-adatom interactions. The results are shown in Figs. 6 and 7, which show the phase diagrams of the system in the $p_{\text{CO}}-T$ plane. The areas denoted by O correspond to an O phase, i.e., a surface totally covered by oxygen. Similarly the phase called CO corresponds to poisoning by CO. In between one finds, depending on the parameters J_i and (p_{CO}, T) , a mixed reactive CO + O phase, which is bounded by $p_1(T)$ and $p_2(T)$. The boundaries $p_1(T)$ and $p_2(T)$ are lower and upper bounds, respectively, obtained from the simulations. A very detailed study of the transition points was not performed, as instead we concentrated on finding the approximate form of the phase diagrams.

(a) $J_1 = J_2 < 0$: This case is shown in Figs. 6(a) and 6(b). The equilibrium window gets narrower as the temperature is lowered and at a critical temperature T_c it disappears completely. The sign or relative magnitude of J_3 only changes the value of T_c . At higher temperatures $e^{-J_i/T} \rightarrow 0$ and desorption dominates, which can be seen from the increase of p_2 .

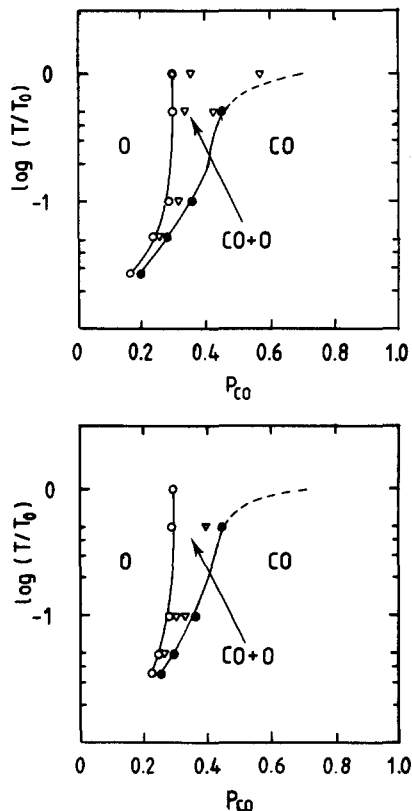


FIG. 6. Phase diagram for the case $J_1 = J_2 < 0$. (a) corresponds to the case $J_1 - J_3 < 0$ and (b) to the case $J_1 - J_3 > 0$. In both cases a critical temperature T_c exists below which the mixed phase cannot be found. (O) = oxygen poisoned surface (\bullet) = CO phase, and (∇) corresponds to a mixed CO + O phase.

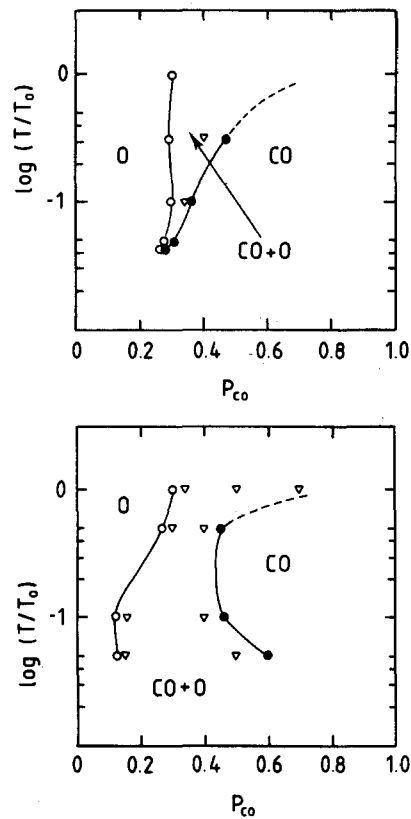


FIG. 7. Phase diagram for the case $J_1 = J_2 > 0$. (a) corresponds to the case $J_1 - J_3 < 0$ and (b) to the case $J_1 - J_3 > 0$. In case (a) there is a critical temperature T_c , whereas in case (b), mixing occurs at all temperatures. Symbols as in Fig. 6.

(b) $J_1 = J_2 > 0$: The behavior of the system is analogous to a two-component equilibrium lattice gas with nn interactions, determined by the sign of $J_1 - J_3$.⁸ If $J_1 - J_3 < 0$, there is again a critical temperature T_c below which the mixed CO-O phase does not exist. On the other hand, if $J_1 - J_3 > 0$, a mixed phase can be found at all temperatures. The two cases are shown in Figs. 7(a) and 7(b). For a two-component (components A and B) lattice gas with interactions J_1 and J_3 between like and unlike atoms, respectively, one obtains by minimizing the free energy $F = U - TS$ of the system for the order parameter $R = p_A - p_B$ [$p_i = N_i/N$ is the probability of finding an atom of type i , ($i = A, B$)],

$$R = \tanh(-\frac{1}{2}\beta\gamma\epsilon R), \quad (10)$$

where γ is the coordination number and $\epsilon = J_1 - J_3$. If $\epsilon < 0$, one finds a critical temperature

$$T_c = -\frac{\gamma\epsilon}{2k_b} \quad (11)$$

below which a mixed phase cannot exist. On the other hand, if $\epsilon > 0$, mixing occurs at all temperatures. In our kinetic model mixing corresponds to the existence of the reactive CO + O phase, i.e., the existence of the equilibrium window, which clearly is absent below T_c , if $\epsilon = J_1 - J_3 < 0$.

IV. CONCLUSIONS

We have studied the catalytic oxidation of carbon monoxide on a platinum surface using two models: (a) an ex-

tended version of the ZGB model and (b) a model which takes into account nn interactions through Boltzmann terms.

In the extended ZGB model we studied the effects of diffusion, desorption (and reaction probability) on the equilibrium window and total reaction rate. The effect of desorption is to randomize the CO distribution on the surface, which leads to a smoothening of the transition at p_2 and the possibility of maintaining a higher CO coverage on the surface. Higher reaction rates can thus be achieved. With increasing desorption the maximum rate is obtained when the coverages are equal, which indicates good agreement with Langmuir-Hinshelwood kinetics and supports the conclusion of a random molecule distribution.

Diffusion causes a shift of p_2 to higher values by decreasing the average CO cluster size. The nature of the transition does not change due to reduced effective diffusion probability with increasing total coverage.

When both diffusion and desorption are present it is clearly seen that desorption is the dominant parameter.

For the interaction model of Sec. III the phase diagrams in the $p_{\text{CO}} T$ plane were obtained. The behavior of the model could be divided into two classes according to whether $J_1 = J_2 < 0$ or $J_1 = J_2 > 0$. In the former case, there always exists a critical temperature T_c , below which the equilibrium window does not exist. In the latter case, however, the sys-

tem behaves analogously to a two component lattice gas and mixing occurs at all temperatures only if $J_1 - J_3 > 0$. If $J_1 - J_3 < 0$, there exists again a critical temperature T_c , below which a reactive phase cannot exist. nn interactions are thus seen to play an active role in the reaction when temperature is lowered. The change in the activation energies becomes dominant at low temperatures and modifies the results obtained with only "topological interactions" at elevated temperatures (the ZGB model).

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