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Effect of lateral interactions on the kinetics of the oxidation of carbon monoxide on palladium

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Monte Carlo simulations are used to study the effect of lateral repulsion between CO molecules on the kinetics of the oxidation of CO and O_2 on a Pd catalyst. The results of CO coverage and reaction rate are compared using three models of lateral interaction: (i) short-range lateral interaction (nearest neighbors); (ii) long-range lateral interaction (dipole–dipole type); and (iii) lateral interaction energy equal to $\beta \theta_{CO}$ mean field approximation (MFA). The results show that the MFA model predicts reaction rates and CO coverage higher than other models. However, the disagreement is significantly less between the MFA model and the long-range lateral interaction model. The results may be interpreted in terms of the different topography of the adsorbed CO phase that is generated when using the various models.

INTRODUCTION

The use of Monte Carlo (MC) simulations has proved to be an excellent method for studying the kinetics of the reaction of CO and oxygen on the surface of noble metals (Pt, Pd, and Rh). The most attractive feature of these simulations is that kinetic parameters that depend on the local characteristics of the surface and the adsorbed phase (different adsorption sites, interactions between neighboring molecules, etc.) can be readily included. In most of the simulations published in the literature[1-7] it has been shown that the kinetics of the oxidation of CO on the metal surface is strongly affected by the nonhomogeneous concentration of the adsorbed CO and oxygen phases. This nonhomogeneity is due to the formation of clusters of oxygen atoms induced by the existence of attractive lateral interactions,[3,4] and also, even in the case of not considering any attraction between oxygen atoms, to the fact that the reaction mechanism on the surface between CO and oxygen leads to the formation of isles of both reactants, thus limiting the reaction to the perimeter of these isles or clusters.[1,2,5-7]

Besides the nonhomogeneity of the adsorbed phase due to the factors mentioned above, the existence of lateral interactions of a repulsive type between the CO molecules adsorbed on the surface of these metals introduces a factor of energy nonhomogeneity of the adsorbed CO molecules. Therefore, the desorption energy of a CO molecule will depend on its surroundings, and the desorption energy of a molecule in the center of a cluster, for example, should be less than that of a CO molecule located in the perimeter of that cluster.

Traditionally it is considered that the effect of the repulsive lateral interactions between CO molecules on their desorption energy causes a linear decrease of the latter as the coverage increases, and it is assumed that the desorption energy E of an adsorbed CO molecule at a given coverage (θ_{CO}) can be calculated by means of the expression

$$E = E_0 - \beta \theta_{CO}, \tag{1}$$

where E_0 is the desorption energy of an isolated CO mol-

ecule, and beta is an empirical parameter that describes the decrease in desorption energy of a CO molecule when it is adsorbed on a surface completely covered with CO ($\theta_{CO} = 1$). Obviously, the above expression does not take into account the fact that the desorption energy of each CO molecule on the surface depends on the surroundings of that particular molecule, but rather it is assumed that the effect of the repulsive lateral interaction is identical for all the adsorbed CO at a given coverage.

A series of interesting papers[8-12] related to the transition phases observed in Ziff et al.'s classical work[2] have shown the influence of different processes (desorption and migration) as well as the existence of interactions between adsorbed species (repulsive or attractive) not considered originally in the ZGB model, on the assumed "active reaction window," i.e., the area in which CO_2 production would be different from zero. The reaction window of the ZGB model is characterized by a lower limit of CO pressure below which the surface becomes poisoned with oxygen (second-order transition), and a higher limit of CO pressure (first-order transition) above which the surface becomes poisoned with CO. In most of the reported simulations the desorption of CO has been considered as a random process with a desorption energy that is independent of coverage,[7,8] or as a process whose desorption energy depends on the interaction with the nearest neighbors.[8,10] Independently of the model, the observed effect of the desorption of CO is the decrease in the size of the adsorbed CO clusters and an increase of the reaction rate, on the one hand, and a smoothening and a spread of the first-order transition on the other, as it prevents complete poisoning of the surface with CO.

This paper reports the use of MC simulations to study the effect of repulsive lateral interactions between CO molecules on the kinetics of the oxidation of CO with oxygen on a Pd surface. Even though the effect of the lateral interaction has been studied,[8,10] it has been considered to be restricted to the nearest neighbors (short-range interaction). In a recent paper Fitchthorn et al.[13] have shown that the lateral repulsive interaction of CO is of the dipole–dipole type, and is therefore of long range. The purpose of this paper is to compare

the results produced by the different models of lateral inter-action already mentioned: short-range lateral interaction, long-range lateral interaction, and the model of lateral inter-action described by Eq. (1). One important motivation for this type of study is determining the magnitude of the error incurred when simplified models such as that of Eq. (1) are used.

MONTE CARLO THEORY AND SIMULATION

The mechanism of the oxidation of CO with oxygen on Pd is open to discussion. Some authors[14,15] have suggested that the reaction occurs between adsorbed oxygen and gas phase CO by means of a mechanism of the Eley–Rideal type. Creighton et al.,[16] however, have shown that the results of experiments at low pressure can be explained by a Langmuir–Hinshelwood (LH) type mechanism, in which the reaction occurs between CO and oxygen species adsorbed on the surface. It is possible that both mechanisms actually oc-cur, and that the contribution of each one depends on the experiment's pressure and temperature conditions.

For simplicity, in this paper it has been assumed that the reaction occurs only via a LH mechanism, i.e., between CO and oxygen adsorbed on the surface. Moreover, the simu-lated system has been simplified by assuming that there is only one species of adsorbed CO, even though it is known that CO can be adsorbed with varying degrees of coordina-tion (linear, bridge, etc.).

The simulated reaction mechanism stages, as well as the kinetic parameters and experimental conditions, are those used by Creighton et al.[16] in their study of the oxidation of CO with oxygen on a Pd catalyst supported on silica.

The MC simulation uses basically a program described in previous publications[6,7] that in this article, has been modi-fied to consider a variable sticking coefficient of CO and the lateral interaction between the adsorbed CO molecules. The simulation algorithm begins with the random selection of an adsorption site on the surface, represented by a 70×70 site matrix. If the chosen site is empty, a decision is made be-tween the adsorption of CO or oxygen by comparing the probability of the occurrence of each of these events with a computer generated random number [0,1]. The occurrence probability of a particular event is determined by dividing the frequency (rate of occurrence per site) of that event by a number (normalization factor) such that the sum of the prob-abilities of all possible events (adsorption, desorption, reac-tion, etc.) is equal to or less than one. The details of the frequency calculation for each process can be found in the references cited, and only the calculation of the adsorption frequencies of CO is shown below, since the evaluation of the adsorption frequency of CO must be carried out differ-ently from the original program. The CO adsorption fre-quency per site is calculated by means of the expression

$$R_{CO} = \frac{P_{CO}}{(2\pi m_{CO} k T_g)^{1/2} N_s} S_{CO}^*,\qquad(2)$$

where S_{CO}^* is a corrected sticking related to the sticking fac-tor (S_{CO}) reported by Creighton et al. by

$$S_{CO}^* = \frac{S_{CO}}{(1 - \theta_{CO} - \theta_{OX})}.\qquad(3)$$

The S_{CO}^* factor is introduced as an artifact in the simulation program to obtain a CO adsorption frequency equivalent to that used in the model of Creighton et al. In our simulation algorithm the term $(1 - \theta_{CO} - \theta_{OX})$ is considered implicitly when a surface site is selected, since the probability that a selected site is empty is equal to $(1 - \theta_{CO} - \theta_{OX})$. In order for the adsorption frequency in the simulation to be that calcu-lated in the model, the value of the sticking coefficient S_{CO} must be artificially incremented dividing it by the $(1 - \theta_{CO} - \theta_{OX})$ term. The validity of this artifact will be shown by the simulations given below. It is important to mention that, because the CO sticking factor is a function of the surface coverage by both reagents, the state of the surface must be calculated by the computer when evaluating the ad-sorption probability for that species.

If the selected site is occupied by CO or oxygen, a de-cision must be made as to whether the adsorbed molecule reacts or is desorbed by comparing the probability of each of these events with a random number. For a reaction to occur, in a neighboring site there must be an adsorbed species dif-ferent from the species present in the chosen site. Once the checking of the selected site is finished, a new site is chosen, and this process is repeated until all the sites in the matrix have been visited, and this is defined as "one interaction step."

In the case of CO desorption, which is the matter of interest in this paper, the desorption probability of a CO mol-ecule is calculated according to the lateral interaction model (short-range and long-range interaction) selected for this simulation.

In the short-range repulsive interaction model it is as-sumed that the interaction is limited to the CO molecules adsorbed on the nearest-neighboring sites. The lateral inter-action energy between two CO molecules adsorbed on neigh-boring sites is assumed to be β/NN, where NN is the number of neighboring sites. In this paper a square grid is used, and NN is therefore equal to 4. Thus, if a CO molecule is com-pletely surrounded by other adsorbed CO molecules (four molecules), the decrease in their desorption energy would be equal to β.

Following Fitchthorn et al.,[13] the image dipole–dipole model is used for those simulations that consider long-range lateral interaction. To evaluate the terms of this model the computer defines a submatrix of 20×20 sites around the checked CO molecule, calculating the contribution of each adsorbed CO molecule within the matrix. The size of this submatrix has been considered adequate for these calcula-tions, since the contribution of CO molecules adsorbed out-side is negligible. For these simulations a value of d (the dipole-image distance) equal to 1 Å is used, and the distance between neighboring adsorption sites is assumed to be 3.2 Å. The value of the static dipole moment is adjusted so that the decrease of the desorption energy of one molecule when $\theta_{CO} = 1$ is equal to β.

The parameter used to study the influence of the differ-ent lateral interaction models on the kinetics of the oxidation
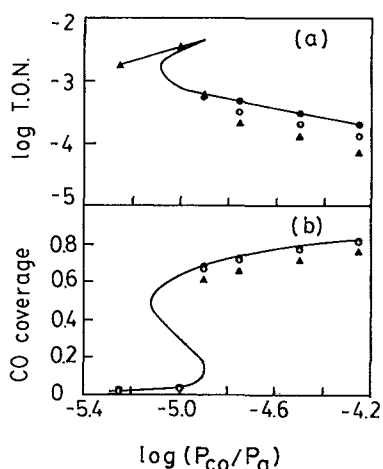
FIG. 1. (a) CO_2 formation rate at 100 °C for different CO pressures and an O_2 pressure of 10^{-5} Pa. (—) analytic solution of the model; (●) MC simulation using the MFA lateral interaction model; (△) MC simulation using the SR lateral interaction model; (○) MC simulation using the LR lateral interaction model. (b) CO coverage under the same conditions used in (a). Same nomenclature as in (a).

of CO with oxygen is the rate of CO_2 production per site per second, i.e., the turnover frequency, or TOF. Its evaluation is done after the system has reached equilibrium for coverage by each reagent, determining the number of CO_2 molecules produced after a certain number of interaction steps (about 5000). The number of CO_2 molecules produced is divided by the number of matrix sites (4900) and by the time equivalent to the number of interaction steps considered. The time equivalent to one interaction step is calculated as described in Ref. 17, comparing the frequency per site of one event in the simulation with its frequency of occurrence in the actual experiment. In this paper the CO desorption frequency for a constant coverage $\theta_{CO} = 1$ is used. Under these conditions the CO desorption frequency is independent of the lateral interaction model under consideration.

RESULTS AND DISCUSSION

The MC simulations were made for a pressure and temperature range similar to that of the experiments of Creighton et al.,[16] i.e., low pressures between 10^{-6} and 10^{-4} Pa, and moderate temperatures between 100 and 150 °C. The simulation begins by considering that the surface is clean, i.e., all the sites are empty. As already mentioned, there is a transition period during which the surface reaches the equilibrium coverage, and after that the TOFs that will appear in the following simulations are calculated.

Figure 1(a) shows the CO_2 production rate (expressed as log TOF) at a temperature of 100 °C and different CO pressures, obtained by solving analytically the model's system of differential equations reported by Creighton et al. The oxygen pressure is kept constant at 10^{-5} Pa. The analytic solution was obtained using the ZPOW subroutine of the IMSL. The corresponding CO coverage is shown in Fig. 1(b). The dependence of the lateral interaction term determined from Eq. (1), which is the same as the one used for the analytic

solution of the model, is equivalent to that obtained from the mean field approximation (MFA),[18] which obviously does not consider the existence of molecules surrounded by different numbers of CO neighbors, but rather assumes an average situation. Later, when Eq. (1) is used to calculate the lateral interaction, the MFA model will be discussed. As Creighton et al. have pointed out, for this pressure and temperature range the kinetics is controlled by the adsorption of one of the reagents. In the low pressure region (relative to the O_2 pressure) the surface is covered mainly with oxygen, and the reaction rate is controlled by the adsorption of CO in the vacant sites. Under these conditions, the CO_2 production rate is first order with respect to the CO pressure. As the CO pressure increases, a point is reached in which the surface starts getting covered with CO, and the kinetics of CO_2 formation is no longer first order, and the TOF decreases as the CO pressure increases. In this region the rate determining step is the O_2 adsorption rate.

In order to check the degree of agreement between the MC simulation and the analytic solution, the reaction was simulated assuming that the CO desorption energy varies with coverage according to the MFA model, i.e., the CO desorption energy is a function of coverage as described by Eq. (1), which is the same function used for the analytic solution of the model. To achieve this, the lateral interaction term $(\beta\theta_{CO})$ is calculated continuously by the computer, and it is assumed that the desorption energy of all the CO molecules adsorbed at a certain coverage decreases by this quantity, independently of the surroundings of each molecule. The results of the rate of formation of CO_2 and the coverage with CO are shown in Figs. 1(a) and 1(b), respectively. It can be seen that both the rate of formation of CO_2 (TOF) and the CO coverage obtained with this simulation agree reasonably well with those predicted by the analytic solution. This makes it possible, on the one hand, to confirm that the artifact used to calculate the CO adsorption probability is correct, and on the other hand that differences that may appear when lateral interaction models different from the MFA model are used would be due only to the model used, and not to disagreement between the analytic solution and the MC simulation. This is not a trivial question since, as reported earlier,[6] different simulation algorithms can lead to different solutions, and it is necessary, therefore, to distinguish between the discrepancies among the analytical solution of a model and the MC simulation due to the algorithm, and those caused by the microscopic model used in the simulation. It is important to note that the pressure range used for CO and O_2 in the simulations corresponds to values that fall within the so-called reactive window. Even though no attempt was made to determine the lower limit of P_{CO} corresponding to the second-order transition, its value is lower than the minimum pressure used in the simulation ($P_{CO} = 3.121 \times 10^{-11}$ Pa). The validity of the result obtained at that pressure was checked assuming a surface with a high oxygen coverage ($\theta_{OX} = 0.85$) as an initial state; this showed that the system evolved to the same state as in the original simulation (which begins with no coverage). It is difficult to specify the upper limit of P_{CO} for the second-order transition because of the inclusion of the CO desorption process.

When the reaction was simulated assuming that the lateral interaction is of the short-range type, the results shown in Fig. 1(a) were obtained for the reaction rate, and in Fig. 1(b) for the coverage with CO. It is seen that the reaction rate obtained from the simulation and that predicted by the analytic solution (and also by the MC simulation using the MFA model) show agreement in the region of low CO relative pressure. In this region the surface is covered with oxygen, and the rate controlling step is, therefore, the adsorption of CO. When the CO pressure is increased and one goes to the region in which the surface is covered with CO, however, it is seen that both the rate of CO_2 production and the CO coverage are lower than those obtained from the MFA model. For the larger P_{CO} value used in the simulation, the reaction rate obtained is 65% lower than predicted by the MFA model. This discrepancy decreases at lower P_{CO}.

If the lateral interaction is assumed to be of the long-range type, the CO_2 production rates and the coverage shown, respectively, in Figs. 1(a) and 1(b) are obtained. The same as in the previous case, there is good agreement between the reaction rates obtained by the simulation and the analytic solution in the low CO pressure region. In the region of higher CO pressures, and when the controlling step is the adsorption of oxygen, the simulation yields a lower CO_2 production rate than that predicted by the analytic solution, even though the CO coverage is the same in both cases. The maximum discrepancy in the reaction rate is obtained for the largest P_{CO} value, which corresponds to maximum coverage with CO (θ_{CO}=0.8). Under these conditions, the reaction rate predicted by the simulation is 30% lower than that obtained with the MFA model. This discrepancy is considerably less than the one obtained with the SR model.

The good agreement shown by the three models of lateral interaction, the MFA, SR, and LR, in the region of low CO relative pressure, when the surface is covered with oxygen, is expected, since in this region the CO coverage is very low, and whichever model of lateral interaction is considered becomes irrelevant. The differences in reaction rates and CO coverage predicted by the different models appear when CO coverage increases. In the case of the short-range (SR) lateral interaction model, the CO coverage in the region of high CO relative pressures, in which the rate controlling step is the adsorption of O_2, is lower than predicted by the MFA model, and a higher reaction rate should be expected because there would be a greater number of vacant sites for the adsorption of oxygen. However, a lower reaction rate is observed than that predicted by the MFA model. In the case of the long-range (LR) model, the CO coverage generated by the MFA and LR models are almost identical, but this is not so for the reaction rates.

These discrepancies in the reaction rates must be attributed to differences in the rates of O_2 adsorption, since this step controls the reaction rate. Since the rate of O_2 adsorption depends on the probability of finding two empty neighboring sites on the catalyst surface, it must be sensitive to the topography of the adsorbed CO phase. Figures 2(a), 2(b), and 2(c) show, for the same CO coverage (θ_{CO}=0.72), the distributions of the CO molecule fractions that have 0, 1, 2, 3, and 4 neighboring CO molecules for the MFA, SR, and LR mod-
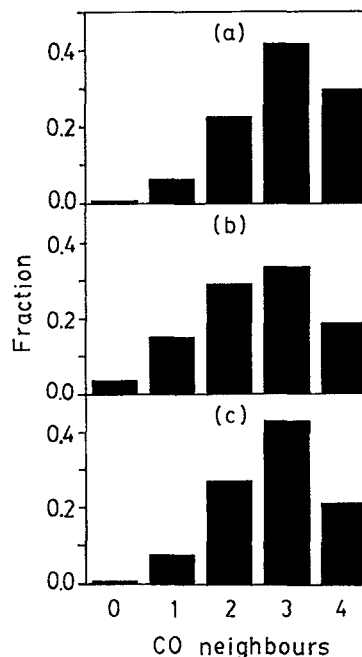

FIG. 2. Fraction of CO molecules with different number of neighboring CO molecules, for a coverage θ_{CO}=0.72. (a) MFA model; (b) SR model; (c) LR model.

els, respectively. These distributions provide information on the topography of the adsorbed CO phase. The greater the displacement of the distribution toward a large number of CO neighbors, the greater the degree of cluster formation. The formation of clusters, i.e., the grouping of CO in large isles on the surface, increases the adsorption rate of O_2,[19] since the number of empty next neighbors is greater than in the case of a more homogeneous CO distribution at the adsorption sites.

In the distributions shown in Fig. 2 it is seen that the distribution most displaced toward a large number of neighboring CO molecules corresponds to that obtained with the MFA model, while the one more displaced toward a low number of neighboring CO molecules is the one obtained with the SR model, and that explains the fact that the latter case yields the lowest CO_2 production rate.

The different distributions shown in Fig. 2 are obviously generated by the lateral interaction model used. In the case of the SR model, the lateral interaction is limited only to the CO molecules adsorbed in sites neighboring the molecule selected by the computer. This will cause the preferential desorption of those molecules surrounded by a greater number of neighbors, thereby decreasing the fraction of molecules surrounded by a large number of neighboring CO molecules.

Something similar, but to a lower extent, happens with the LR model, since in this case a fraction of the surface greater than that of the four neighboring sites of the SR model is considered. With the MFA model, however, all the CO molecules have the same desorption probability, i.e., there is no preferential desorption of the molecules that are surrounded by a larger number of neighbors as compared to
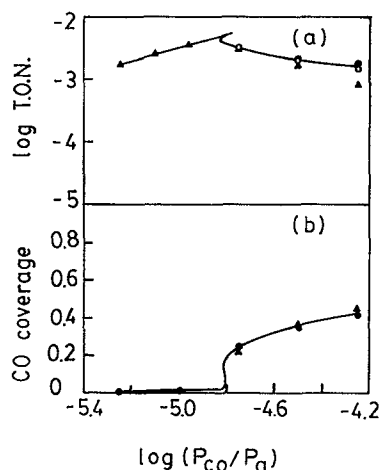
FIG. 3. (a) CO_2 formation rate at 150 °C for different CO pressures and an O_2 pressure of 10^{-5} Pa. Same nomenclature as in Fig. 1(b). (b) CO coverage under the same conditions used in (a). Same nomenclature as in Fig. 1.

other molecules that, in an extreme case, may not have any neighboring CO molecules. This leads to a surface with a larger number of molecules having a great number of neighboring CO molecules compared to the previous cases. It is convenient to point out that although it may be expected that the agreement between the MFA and LR models should be better than with the SR model in relation to CO coverage, it is not trivial when predicting the effect that the different topographies of the CO phase would have on the O_2 adsorption rate.

In the above simulations, the change from a surface covered with oxygen to a surface covered with CO takes place suddenly, leading to high CO coverage. In order to study the effect of the different models of lateral interaction at lower CO coverage, experiments were simulated at 150 °C and the previous CO pressure range and constant O_2 pressure. The results for the reaction rate and CO coverage are shown in Figs. 3(a) and 3(b), respectively. As expected, there is good agreement between all the models in the low CO relative pressure region. In the region of higher CO pressure, and when the controlling step is O_2 adsorption, it is found that the differences in the reaction rates and CO coverage are less pronounced than in the simulations at 100 °C. These results agree with the analysis done previously, and confirm the fact that the differences between the models decrease as CO coverage decreases.

Finally, it is interesting to compare the results of the simulations discussed in this article with the experimental results of Creighton et al. These authors found, from their experiments carried out at 100 °C and a pressure range similar to that of the simulations, that the analytic solution of their model agreed quite well in the low CO relative pressure

region, when the surface is covered with oxygen. As the CO pressure increases and the surface becomes covered with CO, the experimental rate was found to be lower than predicted. This disagreement decreases considerably as the temperature of the experiments increases to 150 °C, and nearly disappears at higher temperatures. Although the aim of this paper is not to ascribe the discrepancies between the model's analytic solution and the experiments, observed by Creighton et al., exclusively to the lateral interaction model used in their work, it should be pointed out that the MC simulations predict, for the simulated system, behavior similar to that observed experimentally.

CONCLUSIONS

The MC simulations presented in this paper lead to the conclusion that the lateral interaction model considered as representing the repulsion between adsorbed CO molecules can result in significant differences in the CO_2 production rate. These differences can be attributed to different topographies of the adsorbed CO phase caused by the lateral interaction model used. Consequently, the validity of Eq. (1) for the calculation of the effect of the lateral interaction is reduced to systems with low CO coverage. Under these conditions, the lateral interaction model does not appreciably affect the CO_2 production rate. For the simulated experimental conditions it was found that Eq. (1) agrees well with the results of the simulations for θ_{CO} values lower than 0.4. It should be noted, however, that the disagreement between the model's analytical solutions and those of the MC simulations for θ_{CO} values greater than 0.4 is significantly less if the long-range lateral interaction model is considered valid.

ACKNOWLEDGMENTS

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