JOURNAL OF CATALYSIS **131**, 369–377 (1991)

NO–CO Reaction on Square and Hexagonal Surfaces: A Monte Carlo Simulation

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Received July 23, 1990; revised January 14, 1991

The NO–CO catalytic reaction on square and hexagonal surfaces is studied through Monte Carlo (MC) simulation. It is shown that the type of the lattice and the dissociation rate r_{NO} of NO to dissociate into N and O are important factors for the reduction (oxidation) of NO (CO). A steady reactive state is achieved only when each site has six nearest neighbors (i.e., a hexagonal surface) and this state exists between two critical concentrations of CO (or NO) for a given value of r_{NO}. The window width of this steady reactive state is largest when $r_{NO} = 1$ and it closes at $r_{NO} \leq 0.8$. It is shown that there is a scaling law between the window width and the dissociation rate. It is further observed that the surface oxygen from NO reacts somewhat less readily with CO than with the oxygen from dissociated O_2, and thus the experimental results previously obtained are confirmed. © 1991 Academic Press, Inc.

INTRODUCTION

An ever-increasing rate of the high consumption of fossil fuel is the main cause of atmospheric pollution. This has prompted many govenments in Europe and the United States to impose severe antipollution regulations. As a result there has been a surge in activity to investigate the reduction of nitric oxide (NO) and the oxidation of carbon monoxide (CO), which are two main polluting gases escaping through automobile exhausts. An efficient procedure for achieving this goal is to coat the exhaust surfaces with some catalytic agent with which the outcoming gases NO and CO react, to form N_2 and CO_2 (*1–4*). The most effective catalyst, so far, is found to be supported rhodium (Rh) metal.

Adsorption and desorption of NO and CO molecules on different metallic surfaces have been studied extensively. Generally, these molecules are adsorbed on transition-metal surfaces with sticking coefficients close to unity (*5*). The CO molecule is adsorbed in its molecular form while, after being adsorbed, the NO molecule is dissociated into N and O at low coverage and with increasing temperature (*6, 7*). Thus, the dissociation rate of CO into C and O is zero while that for NO fluctuates around unity. At a typical operating temperature for a catalytic convertor (700 K) the adsorption of NO results in the liberation of N_2 gas and in the formation of a stable surface oxygen species. These surface oxygen species are then used by CO molecules to be oxidized into CO_2 gas. The simple chemical reaction,

$$NO + CO \rightarrow \tfrac{1}{2}N_2 + CO_2 \qquad (1)$$

is actually rather complex, with the following main steps involved (*2*):

$$CO(g) + S \rightarrow CO(ad) - S \qquad (2)$$

$$NO(g) + S \rightarrow NO(ad) - S \qquad (3)$$

$$NO(g) + 2S \rightarrow N(ad) + O(ad) - 2S \qquad (4)$$

$$NO(ad) + N(ad) - 2S \rightarrow N_2(g) + O(ad) + S \ldots (\delta - N_2) \qquad (5)$$

$$N(ad) + N(ad) - 2S \rightarrow N_2(g) + 2S \ldots (\beta - N_2) \qquad (6)$$

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$$\mathrm{CO(ad)} + \mathrm{O(ad)} - 2S \rightarrow \mathrm{CO_2(g)} + 2S, \quad (7)$$

where (g) and (ad) indicate gaseous and adsorbed states and S represents an empty site.

The above reaction process is a Langmuir–Hinshelwood mechanism. The recombination of two adsorbed N atoms is labeled as producing a $\beta - N_2$ state (i.e., reaction (6)) and the reaction of adsorbed N with adsorbed NO a $\delta - N_2$ state (i.e., reaction (5)). Although the NO–CO reaction has been studied in detail by many experimental methods on different catalytic surfaces (*1, 2, 6–15*), the same cannot be said for theoretical work. Theoretical studies have been made to find the rate of adsorption of reacting agents through the kinetic theory of gases (*2, 16*). Recently the oxidation of adsorbed CO with adsorbed surface oxygen from dissociated O_2 has been simulated by the Monte Carlo (MC) method with very encouraging results (*17, 18*). In the present case the particular electronic structure of the catalytic metal is ignored. It can be included through adsorption and reaction rates of the reacting agents, which will be influenced by the metallic orbitals (and thus the metallic radii). The inclusion of all the possible parameters would make the simulation complicated and time consuming. As a first attempt we keep the study very simple but show that a real insight can be obtained for a catalytic reaction through simulation.

In this paper we apply the MC simulation method to the NO–CO reaction and illustrate the importance of the coordination number and the dissociation rate r_{NO} of NO in the reduction of NO and the oxidation of CO. The details of the MC simulation applied to catalytic reactions have been previously described (*17–19*) in detail. However, in the next section we give a short account of the model adopted for the NO–CO reaction. After this we present our results on square and hexagonal surfaces for different dissociation rates (r_{NO}). The discussion then follows and conclusions are drawn in the final section.

MODEL

The MC method applied to investigate irreversible surface catalytic reactions and models employed are simple (*17–20*). For the NO–CO reaction, we consider two diatomic gases of concentrations X_{NO} and X_{CO} in an infinite reservoir. The total concentation is normalized to 1 (i.e., $X_{NO} + N_{CO} = 1$). For the present study we have considered two types of surface. First, a square surface with four nearest neighbors to each lattice site is considered, then the work is extended to a hexagonal surface where each lattice site then has six nearest neighbors. A hexagonal surface can be easily mapped on a square lattice (*18*). Throughout we use a 40×40 lattice size and employ periodic boundary conditions. We start with an empty lattice.

A trial begins with a random collision of a gas molecule on a square or hexagonal lattice that represents the surface. The colliding molecule is chosen to be CO with a given probability X_{CO} and NO with probability $1 - X_{CO}$, where X_{CO} is the CO concentration in an infinite reservoir. The relative concentrations of CO and NO remain constant throughout the simulation process. If the colliding molecule is CO, the following steps are taken: (i) A site on the lattice is chosen at random. (ii) If that site is already occupied the trial ends (the CO bounces back to the reservoir). (iii) If the site is empty, the CO adsorbs. This is the reaction step

$$\mathrm{CO(g)} + S \rightarrow \mathrm{CO\,(ad)} - S. \quad (2)$$

(iv) The nearest neighbors (nn) to this site are checked randomly. (v) If an O(ad) is found in any of these nn sites, CO_2(g) is formed and two sites are vacated through the reaction step

$$\mathrm{CO(ad)} + \mathrm{O(ad)} - 2S \rightarrow \mathrm{CO_2(g)} - 2S. \quad (7)$$

If the colliding molecule is NO, one of the following two happens: (1) NO dissociates into N and O, or (2) it stays in its molecular form. For this we choose a random number ρ between zero and one. If ρ is less than the dissociation rate (r_{NO}) of NO, the NO molecule dissociates into N and O; otherwise it stays as a molecule. In the first case: (i) two adjacent sites are randomly chosen. (ii) If either of the two is occupied the trial ends, otherwise (iii) N and O are adsorbed through reaction step

$$NO(g) + 2S \rightarrow N(ad) + O(ad) - 2S. \quad (4)$$

(iv) The nn of O(ad) site are checked randomly. (v) If CO(ad) is found in any of nn sits, $CO_2(g)$ is formed and it desorbs leaving behind two empty sites through reaction step (7) as explained above. Now, (vi) the nn of N(ad) sites are checked randomly. (vii) If another N(ad) is encountered in one of nn sites, $N_2(g)$ is immediately formed and two vacant sites are created. This is the $\beta - N_2$ state or the reaction step

$$N(ad) + N(ad) - 2S \rightarrow N_2(g) + 2S. \quad (6)$$

(viii) If during this random check of nn sites to N(ad) one encounters NO(ad), (ix) again $N_2(g)$ is formed (i.e., $\delta - N_2$ state), O(ad) is left in place of NO(ad) and an empty site is created. This represents the reaction step

$$NO(ad) + N(ad) - 2S \rightarrow N_2(g) + O(ad) + S. \quad (5)$$

(x) A further check of nn sites to O(ad) is made randomly to see if step (7) will take place.

In the second case when NO is not dissociated, (i) a site is picked randomly. (ii) If it is occupied, the trial ends, otherwise, (iii) NO is adsorbed through reaction step

$$NO(g) + S \rightarrow NO(ad) - S. \quad (3)$$

(iv) A random check of nn sites is made, and (v) if N(ad) is encountered the step (5) takes place as explained above with the formation of $N_2(g)$, O(ad) and a vacant site. (vi) The nn of O(ad) are checked randomly. (vii) If CO(ad) is encountered, the reaction step (7) follows.

The model with different reaction steps is illustrated in Fig. 1. We show the instant pictures of the catalytic surface at different stages of the reactions. From one surface to the next, we indicate the reaction steps with arrows and numbers. For a given value of r_{NO} we try to find a critical concentration X^C_{CO} of CO such that the surface is not poisoned and we obtain a steady production of N_2 and CO_2. The surface is said to be poisoned when it is completely covered with a mixture of nonreacting O, N, NO, CO atoms and molecules and the catalytic reaction stops. The results obtained are presented in the next section.

The model has been greatly simplified. We consider that the sticking coefficient for CO as well as for NO is unity. This seems to be reasonable when compared with experimental data (*5*). The diffusion of the reacting agents on the surface is ignored. The temperature-related effects are not considered. Various interatomic and intermolecular reactions apart from those involved in the formation of N_2 and CO_2 are ignored. For all the reactions the reaction rate is assumed to be unity. Finally, it is assumed that the adsorbed species do not desorb as such. In spite of such simplifications the results obtained in the case of the $CO–O_2$ reaction were quite helpful in understanding qualitatively the reaction process (*17, 18*). In the present work, as seen later, the simplified model brings clearly into evidence the importance of the catalytic surface and the dissociation rate r_{NO} for the reduction of NO and the oxidation of CO.

RESULTS

If we compare the NO–CO reaction with $CO–O_2$, we find that some NO remains undissociated on the surface, apart from splitting of NO into N and O. The adsorbed nitrogen atoms combine to form $N_2(g)$ + O(ad). Looking into the reaction steps (2)–(7), it is obvious that step (4) is a necessary condition for the reduction of NO and the oxidation of CO with the surface oxygen

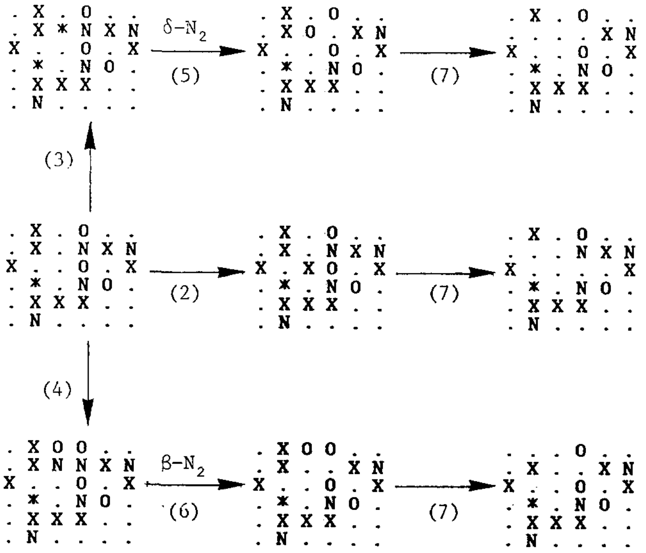
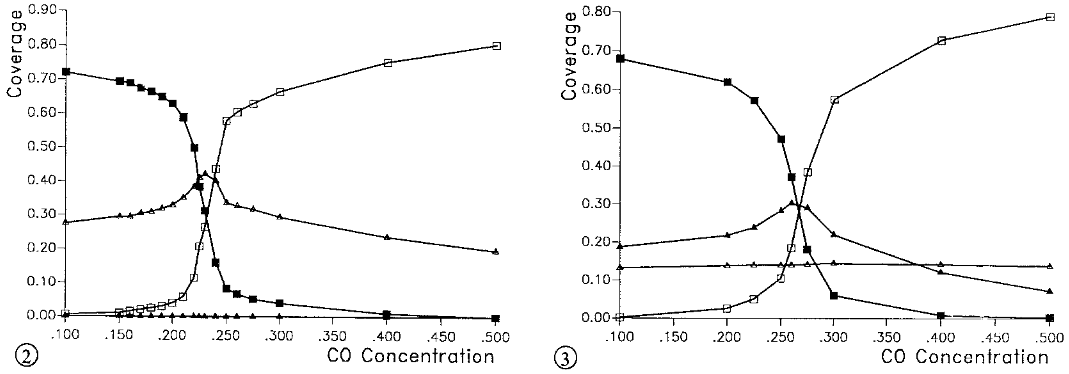


FIG. 1. A schematic representation of different reaction steps as mentioned in the text. O, N, X and * are the adsorbed oxygen, nitrogen, CO and NO respectively. The points (.) are the empty sites. Reaction directions are indicated by arrows and the numbers associated with arrows are the reaction steps.

generated in this step. The most favorable condition to obtain a continuous flow of N_2 and CO_2 is when $r_{NO} = 1$. For a given value of r_{NO} we try to find a nonpoisoned state by varying the relative concentratrions of CO and NO in the reservoir. Generally, we need only a few MC cycles (e.g., fewer than 500 MC cycles) to see if the poisoning takes place. Near the critical concentration we must extend the calculation to 50000 and sometimes even more MC cycles to obtain a precise value of X_{CO}^{C} and to be sure that a steady reactive state (SRS) is obtained. Once this SRS is achieved we calculate the average value of the production of N_2 and CO_2 per MC cycle.

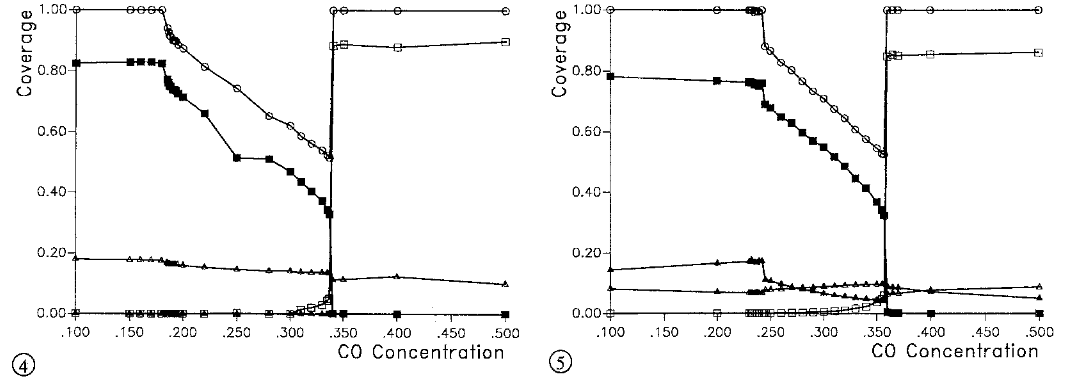
Figures 2 and 3 present the NO–CO reaction on a square lattice for $r_{NO} = 1$ and 0.9, respectively. We note that even for $r_{NO} = 1$ the surface is always poisoned, i.e., the surface is completely covered with a mixture of nonreacting O, CO, and N. The fraction of adsorbed oxygen atoms reduces gradually with the increase of X_{CO}. At about $X_{CO} \simeq 0.225$, there is a sudden fall in this coverage, from 0.625 to 0.1 with a change in X_{CO} from 0.2 to 0.25. Beyond $X_{CO} = 0.25$ the oxygen coverage gradually falls to zero. There is a corresponding but opposite change in the coverage of CO. The nitrogen coverage shows a peak at $X_{CO} \simeq 0.225$. For all values of X_{CO} the total coverage of adsorbed species remains unity and consequently there is no continuous production of either N_2 or CO_2. For $r_{NO} = 0.9$ (Fig. 3), the sharp transition in the coverages of CO and O slightly broadens, while the peak in the nitrogen coverage is replaced by a peak in the NO coverage. The peak position shifts a little to the higher values of X_{CO}. The nitrogen coverage decreases gradually. It seems to form an almost constant background. A further decrease in r_{NO} enhances the abovementioned effects.

After an unsuccessful attempt to obtain a SRS on a square catalytic surface, we increased the coordination number for each site to six. Figures 4 and 5 show the results for $r_{NO} = 1$ and 0.9 on a hexagonal surface. Now the situation changes dramatically. We

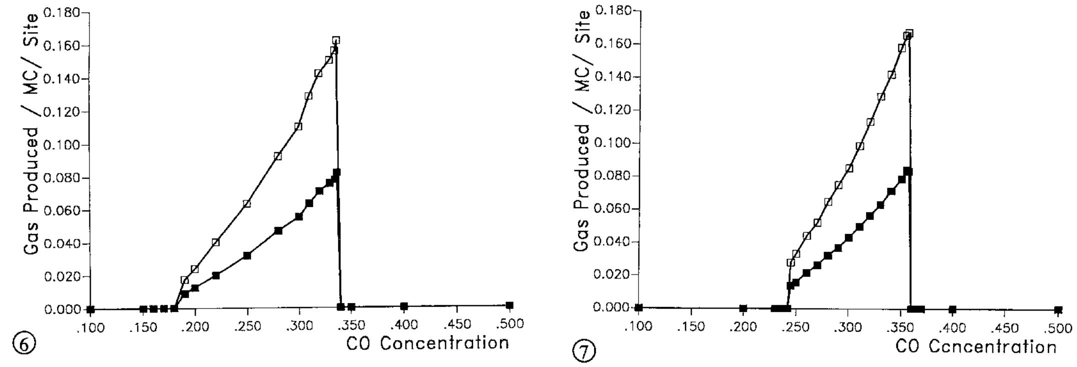


FIGS. 2 AND 3. Coverage of a square lattice as a function of CO concentration for r_{NO} = 1 (Fig. 2) and r_{NO} = 0.9 (Fig. 3). (■) Coverage by O, (△) coverage by N, (□) coverage by CO, (△) coverage by NO. Total coverage (i.e., O + CO + N + NO) is always 1.

see that there is a range of critical concentrations for the SRS. At low concentration of CO, the surface is mainly poisoned by the adsorbed oxygen. For r_{NO} = 1 (Fig. 4), oxygen coverage drops suddenly from a constant value of about 0.83 to 0.76 at $X_{CO} \simeq 0.185$. This drop becomes more gradual until at $X_{CO} \simeq 0.338$ it suddenly goes to zero. The values of critical concentrations reported in the present work have an error of ±0.002 (i.e., $X_{CO} \simeq 0.338 \pm 0.002$). This ±0.002 error is simply due to the fact that the variation in X_{CO} at the critical point for its determination is made with a step of 0.002 and thus we estimate that the maximum error maybe ±0.002, although it might be less. The error is numeric. The CO coverage increases very gradually from zero and suddenly goes from 0.05 to 0.88 at $X_{CO} \simeq 0.338$. These two critical points are referred as X_1 (i.e., $X_{CO} \simeq 0.185$) and X_2 (i.e., $X_{CO} = 0.338$). We note that after X_1 the change in the coverage rate is gradual while at X_2 it is sudden and abrupt. The situation is like that in the CO–O_2 reaction (*17, 18*). At X_1 we observe a second-order phase transition whereas at X_2 it is of the first order. Between these two critical points there is a steady production



FIGS. 4 AND 5. Coverage of a hexagonal lattice as a function of CO concentration for r_{NO} = 1 (Fig. 4) and r_{NO} = 0.9 (Fig. 5). (■) Coverage by O, (△) coverage by N, (□) coverage by CO, (△) coverage by NO, (○) and total average O + CO + N + NO.



FIGS. 6 AND 7. N_2 (■) and CO_2 (□) produced per MC per lattice site on a hexagonal surface at a steady reactive state at different CO concentrations for $r_{NO} = 1$ (Fig. 6) and $r_{NO} = 0.9$ (Fig. 7).

of N_2 and CO_2. This range (X_2–X_1) is referred to as a window Δ.

The decrease in r_{NO} to 0.9 (Fig. 5) has the effect of making the transition at X_1 more gradual. It also takes place at a slightly higher value (i.e., $X_1 \simeq 0.242$). The first-order transition point X_2 is now at 0.360. The steady production rates of CO_2 and N_2 are presented in Figs. 6 and 7 for $r_{NO} = 1$ and 0.9, respectively. For a better understanding, in Fig. 8 we show how the critical points X_1 and X_2 and also the window width Δ of SRS change with decreasing r_{NO}. The window closes at $r_{NO} = 0.8$. The behavior of the window width near the critical dissociation rate $r_{NO} = 0.8$ has been studied in detail and presented on a log–log scale in Fig. 9. In the next section these results are discussed in detail.

DISCUSSION

The simulation of the NO–CO reaction on a square lattice, for all values of r_{NO}, always gives a poisoned state and thus is not an interesting case. A similar study of the CO–O_2 reaction (*17, 18*) gives a window for the SRS. In this latter reaction, the dissociation of O_2 into two surface oxygen atoms enhances the oxidation rate of CO and thus provides for the creation of empty sites, as compared to the NO–CO reaction. The same effect is also responsible for a window width of the SRS on a hexagonal surface for the CO–O_2 reaction (*18*) larger than the corresponding NO–CO reaction. Ziff *et al.* (*17*) obtained the critical points $X_1 \simeq 0.389 \pm 0.005$ and $X_2 \simeq 0.525 \pm 0.001$ on a square lattice (128 × 256) for the CO–O_2 reaction giving a window width $\Delta \simeq 0.136 \pm 0.006$. On a much bigger lattice (512 × 512), Meakin and Scalapino (*18*) later obtained $X_1 \simeq 0.3875$, and $X_2 = 0.5277$ and $\Delta \simeq 0.1402$. Their enlarged window is due to a higher value of the X_2 critical point. On a similar lattice Ziff *et al.* (*17*) also obtained $X_2 \simeq 0.527$ but they rejected this value because they stopped at 10000 MC cycles which they considered not long enough to be sure that a steady state was achieved. On a hexagonal lattice (512 × 512) for the CO–O_2 reaction, Meakin and Scalapino (*18*) obtained $\Delta \simeq 0.217$. Comparing these two simulations on square and hexagonal lattices it is observed that on a hexagonal surface ($\Delta \simeq 0.217$) the SRS is enhanced as compared to the reaction on a square lattice ($\Delta \simeq 0.136$). This clearly shows the importance of the coordination. This effect is more obvious in the present case of the NO–CO reaction. For a square lattice we have no continuous reaction at all. We have a steady production of N_2 and CO_2 only when the coordination number is 6. Earlier studies of the CO–O_2 reaction (*17, 18*) and the present study of the

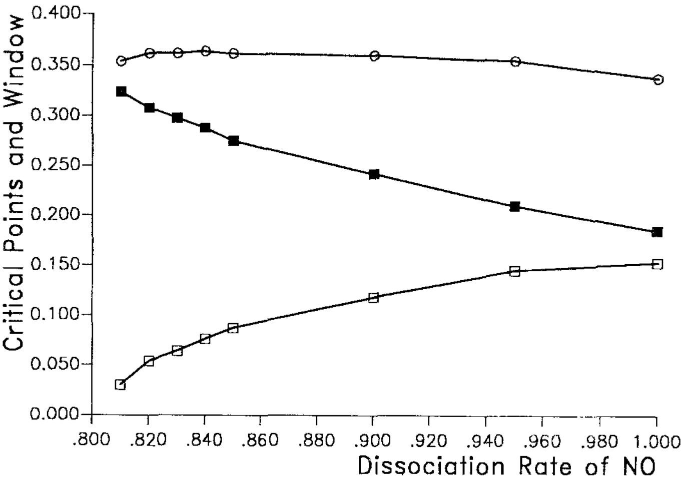


FIG. 8. Critical points X_1 (○), X_2 (■), and the window width $\Delta = X_2 - X_1$ (□) for different values of r_{NO} for the CO-NO reaction on a hexagonal lattice.

NO-CO reaction show that a higher number of neighbors on a catalytic surface is a favorable condition for these catalytic reactions.

Comparing Figs. 2 and 4 for square and hexagonal surfaces for $r_{NO} = 1$ with the corresponding figures (*17, 18*) for the CO-O_2 reaction, it is observed that $\Delta \simeq 0$ and 0.136 for coordination number 4 and $\Delta \simeq 0.153$ and 0.217 for coordination number 6 for the NO-CO and CO-O_2 reactions, respectively. This shows that on either surface the oxidation of CO with the surface oxygen from dissociated O_2 is somewhat more favorable than that from NO. Dubois *et al.* (*8*) and Taylor and Schlatter (*21*) reached the same conclusion under identical experimental conditions for the two reactions involved.

Once a SRS is achieved, we obtain a continuous production of N_2 and CO_2 gases, but this production is not the same throughout

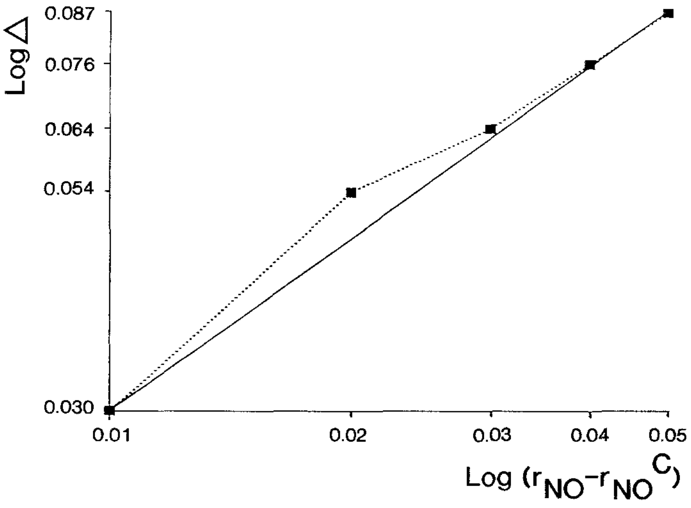


FIG. 9. Log Δ versus log $(r_{NO} - r_{NO}^C)$.

the window width Δ. The steady production starts at the lower critical point X_1 and keeps on increasing gradually until it reaches a maximum, after which it falls abruptly to zero at the first-order transition point X_2. The most efficient production of N_2 and CO_2 takes place at the concentrations close to but less than X_2. Figures 6 and 7 present the escape of N_2 and CO_2 per MC cycle per lattice site once the SRS is achieved for $r_{NO} = 1$ and 0.9, respectively. From these figures it is easily noted that the production of CO_2 is almost two times more important than that of N_2 for a given X_{CO}. For $r_{NO} = 1$, the $\delta - N_2$ state is absent, while for $r_{NO} = 0.9$, it is almost negligible as compared to the $\beta - N_2$ state. It can therefore be assumed that the N_2 is basically produced through the $\beta - N_2$ process. Two adsorbed NO molecules will give two N and two O atoms. The two adsorbed N atoms will give one N_2 molecule if they are sitting next to each other while two surface oxygen atoms may produce two CO_2 under favorable conditions. This explains quantitatively the higher production (roughly two times) of CO_2 as compared to that of N_2.

We show the two critical points X_1 and X_2 and their differences $X_2 - X_1 = \Delta$ for different values of r_{NO} in Fig. 8. There are small variations in X_2 values as a function of r_{NO}, but on the whole it can be said that X_2 is almost constant. On the other hand X_1 starts with a small value of 0.185 ± 0.002 at $r_{NO} = 1$ and increases as r_{NO} decreases until it coincides with X_2 at $r_{NO} = 0.8$, where ultimately the window is closed. Due to a very negligible variation in X_2 as compared to that in X_1, the Δ versus r_{NO} curve is almost a mirror reflection of the X_1 curve. Since the window closes slowly as we reach a critical rate of dissociation $r_{NO}^C = 0.8$, this can be further studied for its behavior as a second-order phase transition. If the relation between Δ and r_{NO} at the critical point is

$$\Delta \,\alpha\, (r_{NO} - r_{NO}^C)^{\eta} \quad r_{NO} \geq r_{NO}^C, \tag{8}$$

it is easy to obtain the exponent η with the help of a log–log plot. Figure 9 shows log Δ versus log $(r_{NO} - r_{NO}^C)$ for r_{NO} very close to r_{NO}^C. From this figure the value of the exponent $\eta \simeq 0.67$ or $\frac{2}{3}$. A further linear graph between Δ and $(r_{NO} - r_{NO}^C)^{2/3}$ gives the constant of proportionality $\frac{2}{3}$ as well. The above relation (8) can be written as

$$\Delta \simeq \frac{2}{3}(r_{NO} - r_{NO}^C)^{2/3}. \tag{9}$$

We note that all the points in Fig. 9 lie on a straight line traced by this relation except the point for $r_{NO} = 0.82$. Although it is possible to improve the situation by further simulation with a higher number of iterations, we have preferred to leave it as it is because the MC simulation is indeed a theoretical experimentation! Our work does show that the transition from open to closed window is a second-order transition and obeys a scaling law.

CONCLUSION

This MC simulation study establishes the importance in the NO–CO catalytic reaction of a high number of the neighbors to obtain a steady flow of N_2 and CO_2. On a hexagonal surface, the SRS starts at a critical concentration X_1 of CO and stops at a higher concentration X_2. The two critical concentrations X_1 and X_2 are second- and first-order transition points, respectively. The difference $\Delta = X_2 - X_1$ is defined as a window for the SRS. This window width decreases as the rate of dissociation r_{NO} of NO decreases, until at a critical value 0.8 it closes entirely. The behavior of the window near the critical dissociation rate on a hexagonal surface has been studied in detail. The window width Δ and the rate of dissociation near the critical point (i.e., $r_{NO} - r_{NO}^C$) obey a scaling law and the exponent is found to be $\frac{2}{3}$.

The present model is basically very simple, and the limitations are given in a previous section. In spite of all the simplifications the model provides a qualitative picture of the NO–CO catalytic reaction. At the same time it opens a future perspective in this domain. It is possible to simulate other chemical reactions and make a comprehensive study of the possible effects of the geometry of the surfaces. Different reaction paths can be simulated to see the possible final products and by-products.

A very interesting observation is that the inherent rate of the CO–O_2 reaction on a catalytic surface is much higher than that of NO–CO. Rate measurements (*9*) over an alumina-supported Rh (Rh/Al_2O_3) in CO–NO–O_2 mixtures have shown, however, that the presence of a small amount of NO in the reactant stream prevents the occurrence of the CO–O_2 reaction until the extent of NO–CO reaction becomes significant. On the other hand similar experiments with Pt/Al_2O_3 catalysts (*10*) have shown that the CO–O_2 reaction is much less affected by the presence of NO than with that of Rh/Al_2O_3. It is evident that the adsorption characteristics of CO and NO on the two surfaces are different. NO is the dominant species present on Rh while Pt is predominantly covered with CO (i.e., relatively low NO coverage). This particular reaction CO–NO–O_2 will be an interesting candidate for simulation to elucidate the effect of different adsorption characteristics of the reactants in a catalytic process.

At present our calculations for square and hexagonal surfaces are based on a 40 × 40 lattice size. We have not made a detailed study of the size effect. Ziff *et al.* (*17*) produced satisfactory results with a lattice size 128 × 256, while studying CO–O_2 reaction on a square lattice. By increasing the lattice size to 512 × 512 they reached the same conclusion. The absence of the size effect on the phase transition critical points on different types of surfaces in the CO–O_2 reaction is clearly established by Meakin and Scalapino (*18*). Thus, the present simulation of the NO–CO reaction on a 40 × 40 lattice size may be considered stable and trustworthy.

The CO–O_2 system has been studied quite extensively both analytically (*22, 23*) and by MC simulations (*17, 18*). Mean field theories (*22, 23*) by and large predict the phase diagram correctly. The NO–CO reaction is more complicated, and both computer simulation and analytical studies had been lacking. The presence work partially fills this gap.

ACKNOWLEDGMENTS

It is our pleasure to thank Drs. A. Sadiq and F. Garin for many useful discussions.

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