NO-CO surface reaction on a square lattice

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A Monte Carlo simulation of the NO-CO catalytic reaction on a square lattice is presented. It is shown that a steady reactive state for this reaction exists when the adsorbed N atom is allowed to diffuse on the surface. The window width of this reactive state diminishes as the diffusion rate decreases. The power law behavior of the window width against the diffusion rate has a critical exponent 1/3.

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I. INTRODUCTION

An investigation of lattice models of catalytic surface reactions has been extremely helpful in gaining a better insight into the kinetics of catalytic processes [1–3]. Ziff, Gulari, and Barshad introduced a monomer-dimer model to describe the oxidation of CO on metal surfaces. Parallel to Ziff *et al.* [4], Dumont *et al.* [5] also used the same model to study a general monomer-dimer reaction. This model is generally called as ZGB model. In this model CO adsorbs onto a single vacant surface site while O_2 needs two adjacent vacant sites for adsorbtion. Nearest neighbor pairs of O-CO combine to form CO_2, which desorbs, leaving behind two vacant sites. The only parameter in this model is the feed concentration y of CO. As a function of y, the system exhibits two irreversible phase transitions. A second-order phase transition at $y_1 = 0.389 \pm 0.001$ separates an oxygen poisoned state from a steady reactive state (SRS) while a first-order phase transition at $y_2 = 0.525 \pm 0.001$ separates a CO poisoned state from a SRS. Within the window defined by $y_1 < y < y_2$ the system exhibits a SRS with a continuous production of CO_2.

The effects of diffusion and desorption of CO on the ZGB model has been studied by various authors [6–8]. These two mechanisms are observed to have no effect on the second-order phase transition point y_1. The diffusion of CO increases the reaction rate, with, as a result, a clear-cut shift of the first-order transition point y_2 toward higher values, thus increasing the window width of the reactive state. The desorption of CO slows and delays the saturation of the surface by CO, resulting in a smoothening and spread of the first-order transition. Meakin and Scalapino [9] investigated the effect of the lattice type on the reactive window of the ZGB model. They found that for a hexagonal lattice the reactive window increases in size as compared to the usual square lattice with $y_1 = 0.360 \pm 0.005$ and $y_2 = 0.561 \pm 0.001$. This reaction has also been studied in the SRS for individual covering rates for their analytical behaviors as a function of CO concentration [10].

Based on the ZGB model, other lattice models were later introduced to simulate different catalytic surface reactions. The dimer-dimer model to simulate the reaction $(1/2)A_2 + B_2 \longrightarrow AB_2$ was studied by Albano [11]. Without diffusion of the lighter species B the system exhibits a first-order transition at $y_{B2} = 2/3$, separating an $A+AB$ poisoned state from a B poisoned state. The introduction of diffusion of B atoms does not change the above picture quantitatively. However, diffusion combined with desorption of two B atoms (i.e., B_2) produces a SRS for $y > 0.0$. More recently, Yaldram and Khan [12] have studied the dimer-dimer catalytic surface reaction of the type $AB + C_2 \longrightarrow (1/2)A_2 + C_2B$. This mimics the reaction NO + $H_2 \longrightarrow (1/2)N_2 + H_2O$. They found that the diffusion and desorption of the lighter atom C (H) does not produce a SRS. However, a slight movement of A (N) plays a very crucial role in taking the system from a poisoned state to a SRS. The diffusion probabilities D_A of A (N) were varied from 1.0 to 0.001. Even for $D_A = 0.001$ the SRS persists without a change of width of the reaction window, but with lower production rates for A_2 (N_2) and C_2B (H_2O).

Another more realistic monomer-dimer reaction of the type NO + CO $\longrightarrow (1/2)N_2 + CO_2$ has been studied by Yaldram and Khan [13,14] and other authors [15,16]. These studies show that for this particular reaction the existence of SRS is linked with the type of lattice. A square lattice results in a final poisoned state for all feed concentrations of CO while a hexagonal lattice (each site surrounded by six nearest neighbors) shows a SRS. For complete dissociation of NO the second-order transition occurs at $y_{CO} = y_1 = 0.1185 \pm 0.001$ and the first-order transition at $y_2 = 0.354 \pm 0.001$. The dissociation rate of NO (R_{NO}) also plays a crucial role in determining the window width for SRS. The reactive window narrows as one gradually decreases the rate of NO dissociation until for about $R_{NO} = 0.80$ the SRS completely vanishes.

It is clear that the lattice type, desorption, diffusion,

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dissociation, etc. can all affect different reaction models in different ways. Either one or a combination of two or more of these factors may help in producing a steady reactive state in reactions which otherwise end up in a poisoned state. The objective of this study is to show that in the NO-CO surface reaction model one can generate a steady reactive state on a square lattice by introducing diffusion of an appropriate species. To this end, we have undertaken a systematic study of the influence of diffusion of the three species (CO, O, and N) on the kinetics of the reaction on the square lattice.

II. MODEL AND SIMULATION

The details of the model and simulation procedure have been discussed elsewhere [13]. Here we reproduce only the important features. The mechanism for the simultaneous catalytic reduction of NO and oxidation of CO is believed to proceed via the following Langmuir-Hinshelwood mechanism [17]:

$$\mathrm{CO}(g) + S \longrightarrow \mathrm{CO}^S, \tag{1}$$

$$\mathrm{NO}(g) + S \longrightarrow \mathrm{NO}^S, \tag{2}$$

$$\mathrm{NO}(g) + 2S \longrightarrow \mathrm{N}^S + \mathrm{O}^S, \tag{3}$$

$$\mathrm{N}^S + \mathrm{N}^S \longrightarrow \mathrm{N}_2(g) + 2S, \tag{4}$$

$$\mathrm{NO}^S + \mathrm{N}^S \longrightarrow \mathrm{N}_2(g) + \mathrm{O}^S + S, \tag{5}$$

$$\mathrm{CO}^S + \mathrm{O}^S \longrightarrow \mathrm{CO}_2(g) + 2S, \tag{6}$$

where S indicates an empty site, $A(g)$ an A atom in its gaseous phase, and A^S an A atom when it is adsorbed on an active site S.

The CO molecule is adsorbed in its molecular form (step 1). The NO molecule may adsorb in its molecular form (step 2) or may dissociate into its constituents (step 3). Two adsorbed N atoms can recombine to form $N_2(g)$ (step 4), while the undissociated NO^S can also react with the dissociated N^S to form $N_2(g)$ (step 5). Finally, the CO^S reacts with O^S to form $CO_2(g)$ (step 6).

In the present study, since we consider complete dissociation of NO, steps 2 and 5 are ignored. In the simulation, a square lattice of linear dimension $L = 40$ represents the surface. The surface is in contact with an unlimited supply of CO and NO. The sum of the partial pressures of the gases is normalized to one ($y_{CO} + y_{NO} = 1$). A CO or NO molecule is chosen with a probability proportional to its partial pressure. A surface site is also chosen at random. If the site is occupied, the trial ends; otherwise one of the following two possibilities can take place. (i) If CO had been initially selected, this is adsorbed onto the vacant site. Its nearest neighbors are scanned randomly for the presence of O^S. In the case O^S is located, $CO_2(g)$ is formed, which desorbs, leaving behind two vacant sites. (ii) If the initial selection is that of NO, in that case a neighboring site of the empty site is picked up randomly. If the site is occupied, the trial ends; otherwise the NO is dissociatively adsorbed onto the two empty sites. The choice of which site is occupied by N or O is made randomly.

Once N and O are adsorbed, the nearest neighbors of each are scanned for the presence of N^S or CO^S, respectively. In the first case $N_2(g)$ is formed and in the second case $CO_2(g)$ is formed and liberated. The diffusion of X (CO, O, or N) is attempted in the following way. If the random selection of a surface site results in the identification of an occupied site, a nearest neighbor of this site is selected randomly. If the site is empty, X is moved to this location with a diffusion probability D_X. After the diffusion the nearest neighbors of the new position are scanned for the possibility of the formation of gas molecule.

The variables in our study are y_{CO} and D_X. Equilibrium coverages are measured as a function of y_{CO} for different diffusion probabilities D_X. The step size for y_{CO} (y) is taken as 0.01, except close to the transition points, where the step size is reduced to 0.001 for a precise determination of the transition points. To locate the critical points, five independent runs, each up to 50 000 Monte Carlo (MC) cycles were carried out. If all five runs proceed up to 50 000 MC cycles without the lattice getting poisoned, the particular point is considered to be in a SRS. The poisoning of even a single run is a sufficient criterion for considering the point in the poisoned state.

III. RESULTS AND DISCUSSIONS

A. Diffusion of CO and O

As earlier attempts to obtain a SRS for the NO-CO reaction on a square lattice failed, we tried in the present work to overcome this difficulty by allowing the reactive agents to diffuse on the surface once they have been adsorbed. The diffusion of CO or O always gives a poisoned state. In Fig. 1, we present the situation when the diffu-

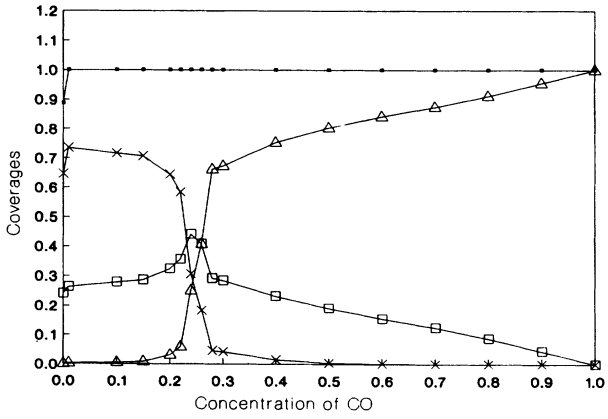

FIG. 1. Coverage rates θ_T (dots), θ_O (crosses), θ_N (empty squares) and θ_{CO} (empty triangles) versus feed concentration y_{CO} when adsorbed CO diffuses on the surface ($D_{CO} = 1$).

sion probability of CO (D_{CO}) is 1. This figure is exactly the same as the one obtained without any diffusion (Fig. 2 in Ref. [13]). The total coverage θ_T is always 1, except when $y_{CO} = 0.0$, where it is about 0.8. Though the surface is always poisoned, there exists a transition point at $y_{CO} = 0.225 \pm 0.001$, where the coverages θ_O and θ_{CO} of O and CO, respectively, cross each other and θ_N has a peak. For $D_O = 1$ we also fail to obtain any SRS and the situation is about the same as when CO was allowed to diffuse, except that the peak in θ_N at $y_{CO} = 0.225 \pm 0.001$ is somewhat broadened.

B. Diffusion of N

Figure 2(a) shows the different coverages as a function of feed concentration (y_{CO}) when $D_N = 1$. Fig. 2(b) presents an enlarged picture between $y_{CO} = 0.15$ and 0.30. From Fig. 2 it is evident that the diffusion of N generates a SRS with a second-order phase transition (SOPT) critical point $y_1 = 0.203 \pm 0.001$ and a first-order phase transition (FOPT) critical point $y_2 = 0.293 \pm 0.001$. Thus the reactive window width is $\Delta = 0.089 \pm 0.002$. For $y < y_1$, $\theta_T = 1$, $\theta_O \simeq 0.78$, $\theta_N \simeq 0.22$, and θ_{CO} is almost zero. These values remain roughly the same until we reach y_1, where θ_O and θ_N start decreasing and θ_{CO} begins to increase. A more important point is that θ_T is less than 1 and the coverage rate of the vacant sites θ_V increases beyond y_1. This tendency persists until we reach the FOPT critical point y_2, where abruptly θ_T becomes 1, θ_{CO} jumps to a large coverage ($\simeq 0.7$) from almost zero, and θ_O drops to a very small value. Only for θ_N there is a small drop and it goes to zero quite smoothly as y_{CO} increases. In abundant CO^S, it is always possible for N^S to sit scattered without getting close to first neighborhood of another N^S to form $N_2(g)$ and to create two vacant sites.

When we reduce D_N to a smaller value, the general

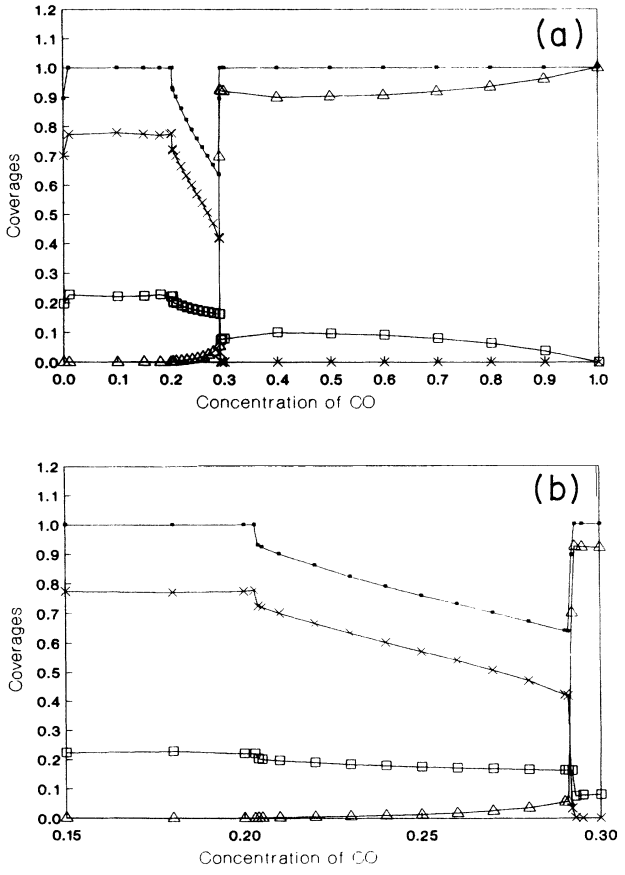

FIG. 2. Coverage rates as in Fig. 1 when (a) adsorbed N is allowed to diffuse (D_N=1) and (b) presented between y = 0.15 and 0.30.

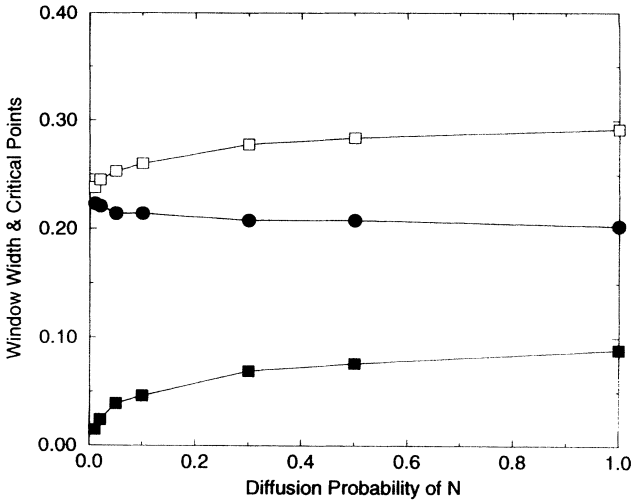

FIG. 3. Window width Δ (filled squares) and critical points y_1 (filled circles) and y_2 (open squares) plotted against D_N.

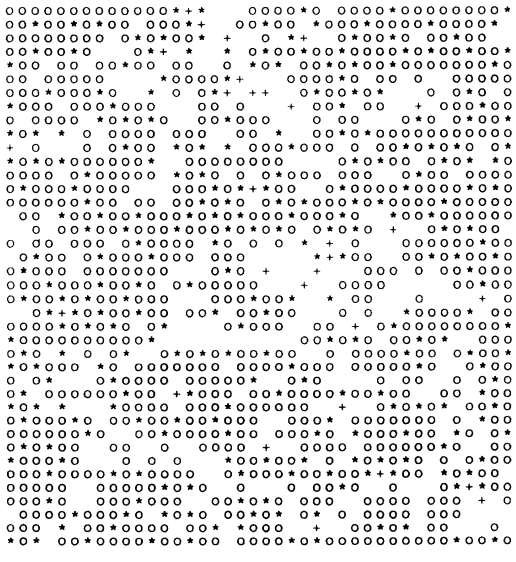

FIG. 4. A snapshot of a SRS when $D_N = 1$ and $y_{CO} = 0.25$. CO^S, O^S and N^S are indicated by pluses, empty circles, and stars, respectively.

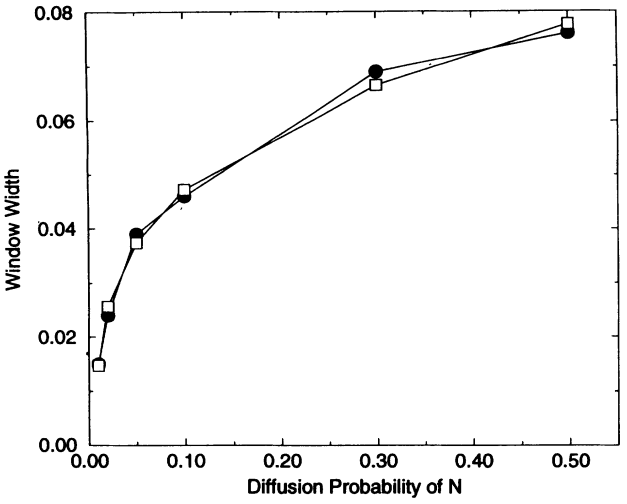

FIG. 5. SRS window width Δ versus D_N, values obtained by Monte Carlo simulation (filled circles) and values obtained by the root mean square fit (open squares).

trend of the different coverages persists, but the critical points change their positions so that the SRS window Δ decreases with the decrease of D_N and eventually it is shut. The points y_1, y_2 and the window width Δ have been systematically obtained for different values of D_N, which we present in Fig. 3 as a function of y_{CO}. In Fig. 4 we present a typical snapshot of the SRS when $D_N = 1$ and $y_{CO} = 0.25$. At y_1 a continuous production of $CO_2(g)$ and $N_2(g)$ starts and keeps on increasing until we reach y_2, where it sudenly stops. The production rate of $CO_2(g)$ is about twice that compared to that of $N_2(g)$ for a given feed concentration.

C. Window Δ and critical points y_1 and y_2

The closing of the SRS window Δ as D_N decreases is an interesting phenomenon and we have studied it to find an analytical relation between the two. From Fig. 3 it seems that there is a power law relation. We obtain a

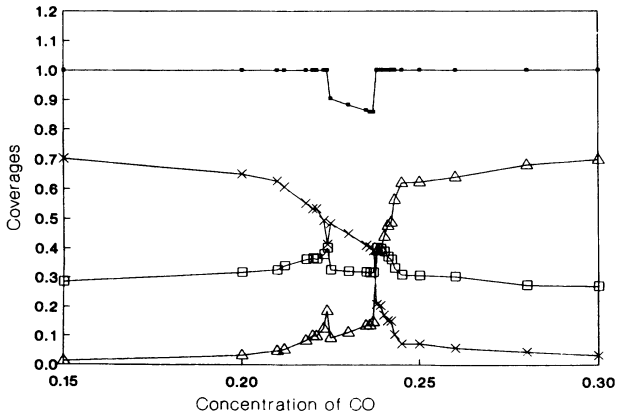

FIG. 6. Same as in Fig. 2(b) when $D_N = 0.01$.

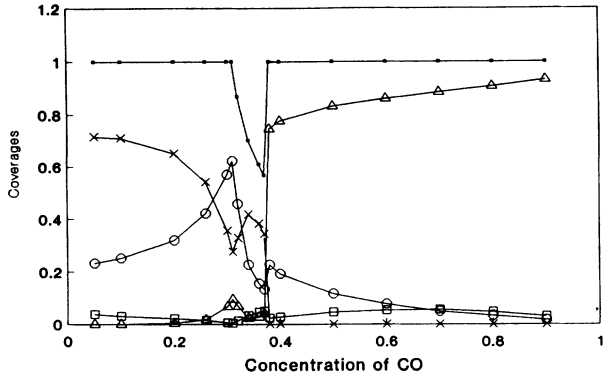

FIG. 7. Same as in Fig. 1, but also θ_{NO} (open circles) when CO-NO reaction is studied on a hexagonal surface and the rate of dissociation $R_{NO} = 0.83$, just before the closing of the SRS window.

simple relation by fitting the root mean square:

$$\Delta \simeq 0.1 D_N^{1/3}. \tag{7}$$

In Fig. 5 we present the points as obtained by simulation (closed circles) and also the ones that we get through the above relation. The agreement is quite satisfactory. A log-log scale of Δ against that of D_N gives a straight line. This shows a second-order phase transition of Δ at $D_N = 0.0$ with a critical exponent 1/3. It will be intersting to point out that while studying the NO-CO reaction on a hexagonal lattice, Yaldram and Khan [13] also found a second-order phase transition of Δ at a critical value of the dissociation rate R_{NO} of NO. In that case the critical exponent was found to be 2/3.

The critical points y_1 and y_2 approach each other as D_N decreases. The critical point y_2 moves more rapidly than y_1. Ultimately, they merge together to shut the SRS window. It is interesting to see how the individual coverages behave as the two critical points come closer. A typical situation is presented in Fig. 6, where $D_N = 0.01$. Looking into individual coverages θ_N, θ_O, and θ_{CO}, we observe some strange behavior at the SOPT critical point y_1. The coverages θ_O and θ_{CO} have maxima while θ_N has minimum at y_1. All these coverages have their first-order derivatives with respect to the feed concentration as zero at y_1. A similar situation was also observed in the case of the NO-CO reaction on a hexagonal surface [13]. For a better comparison with Fig. 6 we present this particular case in Fig. 7, when the dissociation rate of NO (R_{NO}) is 0.83, just close to 0.80 when the SRS vanishes. The similarities between Figs. 6 and 7 are evident. When the SRS eventually vanishes, only for θ_N we still have $(d\theta_N/dy) = 0$ at y_{CO}=0.225. This particular behavior is contrary to the second-order phase transition. It should be recalled that for D_N=0.01 (Fig. 6), θ_T and θ_V still have second-order phase transition characters.

IV. CONCLUSION

The CO-NO monomer-dimer reaction is very different as compared to the more classical CO-O_2 reaction. To

achieve a SRS on a square lattice for the CO-NO reaction, it is necessary to allow the adsorbed N atom to diffuse, whereas no such condition is required in the $CO-O_2$ reaction. The indivdual coverages in the case of CO-NO reaction behave very strangely at y_1 when the SRS window closes. This kind of behavior does not exist in the case of the $CO-O_2$ reaction. Finally, the present study clearly establishes that a high coordination is not a necessary condition to obtain a continuous production of N_2 and CO_2. In view of this observation, the CO-NO reaction should be studied further not only by Monte Carlo simulation but also by other approaches such as mean field theory and surface rate equations.

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[1] P. Grassberger, Z. Phys. **B 47**, 365 (1982).
[2] P. Dickman and M. Burschka, Phys. Lett. A **127**, 132 (1980).
[3] B. Grinstein, Z. W. Lai, and D. A. Browne, Phys. Rev. A **40**, 4820 (1989).
[4] R. M. Ziff, E. Gulari, and Y. Barshad, Phys. Rev. Lett. **56**, 2553 (1986).
[5] M. Dumont, M. Poriaux, and P. Dagonnier, Surf. Sci. **169**, L307 (1986).
[6] H. P. Kaukonen and R. P. Neiminen, J. Chem. Phys. **91**, 4380 (1986).
[7] M. Ehsasi, M. Maltock, O. Frank, J. H. Block, K. Christmann, F. S. Rys, and W. Horschwald, J. Chem. Phys. **91**, 4949 (1989).
[8] E. V. Albano, J. Chem. Phys. **94**, 1499 (1991).
[9] P. Meakin and D. J. Scalapino, J. Chem. Phys. **87**, 731 (1987).
[10] M. A. Khan and K. Yaldram, Surf. Sci. **269**, 476 (1992).
[11] E. V. Albano, J. Phys. A **25**, 2557 (1992).
[12] K. Yaldram and M. A. Khan, J. Phys. A **26**, 6135 (1993).
[13] K. Yaldram and M. A. Khan, J. Catal. **131**, 369 (1991).
[14] K. Yaldram and M. A. Khan, J. Catal. **136**, 279 (1992).
[15] K. Yaldram, K. M. Khan, N. Ahmed, and M. A. Khan, J. Phys. A **26**, L801 (1993).
[16] B. J. Brosilow and R. M. Ziff, J. Catal. **136**, 275 (1992).
[17] Se H. Oh, B. B. Fisher, J. E. Carpenter, and D. W. Goodman, J. Catal. **100**, 360 (1986).