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Kinetic Phase Transitions in a Three-Component NO–CO–O_2 Model for Heterogeneous Catalysis

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A simulation study has been made of the three-component NO–CO–O_2 heterogeneous catalytic reaction, where the three species are adsorbed on a hexagonal lattice (each site having six nearest neighbours (nn)). NO and O_2 are considered to dissociate on adsorption while CO is adsorbed in its molecular form. Nearest adsorbed CO and O react to form CO_2, while N combines with the nearest N to form N_2. The system is studied for different ratios of the feed concentrations, which is varied to keep the total concentration (y) normalised to unity, i.e., $y_{CO} + y_O + y_{NO} = 1$. Different phase transitions and respective stationary states are studied by Monte Carlo (MC) simulation. Many interesting observations are presented. The most interesting outcome of the present study is that the steady reactive state in NO–CO–O_2 reaction has a much larger range than in individual two-component NO–CO and CO–O_2 reactions. © 1994 Academic Press, Inc.

1. INTRODUCTION

Ziff *et al.* (1) introduced an equilibrium model reaction to study the Langmuir–Hinshelwood mechanism for the heterogeneous catalytic reaction in which CO reacts with O_2 to liberate CO_2. This irreversible dimer–monomer (DM) reaction exhibits two phase transitions. For small concentration (y_{CO}) of CO in the gas phase the surface is poisoned (saturated) by oxygen atoms. A steady production of CO_2 starts at the first transition point (y^3_{CO}) and stops at the second transition point (y^4_{CO}). For further increase in CO concentration, the surface becomes poisoned by CO. The positions of the critical points y^3_{CO} and y^4_{CO} are found to be sensitive to the surface morphology (2). The width of the region for which the system exhibits a steady reactive state (SRS) is enhanced for a hexagonal lattice, as compared to a square lattice (each site of the lattice has four nn). The two respective critical transition concentrations are 0.389 and 0.525 for a square lattice and 0.365 and 0.558 for a hexagonal lattice, respectively. Other aspects of this particular reaction have been further studied by many authors (3–9).

Another DM reaction in which NO reacts with CO on a surface has also been studied (10, 11). For this DM system a SRS cannot be sustained on a square lattice (10, 12). However, the two transition points with a corresponding SRS region are obtained on a hexagonal lattice. A second order phase transition (SOPT) takes place at $y^1_{CO} = 0.185$ and a first order phase transition (FOPT) at $y^2_{CO} = 0.338$.

So far these two reactions have been studied separately. Experimentally, it is observed that in general the CO–O_2 reaction is not affected by the presence of a small amount of NO, but there are some exceptional cases where a small amount of NO easily blocks the CO–O_2 reaction (13). Thus, it should be interesting to look into the NO–CO–O_2 reaction to understand the experimental observation. In this work we have tried to investigate this particular three-component reaction in which all the three species NO, CO, and O_2 are present in the system. We have determined the behaviour of this system for different ratios of the feed concentrations of the three components. In the next section we describe the model and the simulation technique employed. In Section 3 we present and discuss the results and finally the conclusions are drawn.

2. MODEL AND SIMULATION

The two-component CO–O_2 reaction is now believed to proceed via the following Langmuir–Hinshelwood mechanism.

$$CO(g) + S \rightarrow CO^S \qquad [1]$$

$$O_2 + 2S \rightarrow 2O^S \qquad [2]$$

$$CO^S + O^S \rightarrow CO_2(g) + 2S \qquad [3]$$

Here (g) and S represent the gas phase and an active site respectively. A^S means that an atom A has been adsorbed on an active site S. A CO gas molecule needs one surface site for its adsorption, whereas an O_2 molecule on adsorption splits into its two constituent atoms and occupies two surface sites. Whenever a CO^S molecule finds itself sitting next to an O^S atom, a CO_2 gas molecule is formed

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which desorbs from the surface leaving behind two active sites.

The two-component NO–CO reaction is slightly more complicated and proceeds via the following mechanism.

$$CO(g) + S \rightarrow CO^S \quad [1]$$

$$NO(g) + S \rightarrow NO^S \quad [4]$$

$$NO(g) + 2S \rightarrow N^S + O^S \quad [5]$$

$$NO^S + N^S \rightarrow N_2(g) + O^S + S \quad [6]$$

$$N^S + N^S \rightarrow N_2(g) + 2S \quad [7]$$

$$CO^S + O^S \rightarrow CO_2(g) + 2S \quad [3]$$

NO(g) can either become adsorbed onto a single site in its undissociated form (step 4) or it may dissociate into its constituents (step [5]) with each atom occupying a different neighbouring site. In what follows we assume that NO is completely dissociated on adsorption, so that we can ignore steps [4] and [6]; the $N_2(g)$ is liberated entirely from a combination of two N^S atoms.

The Monte Carlo simulation technique applied to these two irreversible surface catalytic reactions and the model employed have been discussed quite extensively (1, 2, 5–11). For the two-component XO–CO reaction (where X stands for either O or N) we consider two diatomic gases of concentration y_{XO} and y_{CO} in an infinite reservoir. The total concentration $y_{XO} + y_{CO}$ is normalised to unity. A trial begins with a random collision of a gas molecule with the hexagonal lattice that represents the surface. The colliding molecule is chosen to be CO with a probability y_{CO} and XO with a probability $1 - y_{CO}$. The relative concentrations of CO and XO remain constant throughout the simulation process. If the colliding molecule is CO, then a site on the surface is chosen randomly. If the site is already occupied the trial ends; otherwise CO becomes adsorbed on the surface site. If, on the other hand, the colliding molecule is XO then two neighbouring sites are chosen randomly. If both are empty then X adsorbs on one and O absorbs on the other site, or else the trial ends. Once CO or XO has been adsorbed then nn of each adsorbed site are scanned. If an O is present in the neighbourhood of CO, CO_2 gas is formed, which is desorbed immediately (step (3)). Finally the presence of an X in the vicinity of another X will result in the liberation of an X_2 only if X happens to be N (step 7); this is the only difference between the two DM reactions.

In the above two cases of the two-component reactions, as a function of y_{CO} we have two types of poisoned states: PS1 when $y_{CO} <$ SOPT critical point and PS2 when $y_{CO} >$ FOPT critical point. In between we have a SRS. To study the three-component NO–CO–O_2 reaction we have divided the y_{CO} into five different regions.

(i) Region I: $y_{CO} < 0.185$. In this region both the two-component reactions NO–CO and CO–O_2 give PS1.

(ii) Region II: $0.185 < y_{CO} < 0.338$. In this region two component NO–CO reaction gives a SRS whereas the CO–O_2 reaction gives PS1.

(iii) Region III: $0.338 < y_{CO} < 0.365$. Both the two-component reactions lead to PS. However, the interesting point is that it is PS1 for the CO–O_2 reaction and PS2 for the CO–NO reaction.

(iv) Region IV: $0.365 < y_{CO} < 0.558$. Only the pure CO–O_2 reaction is in SRS while the NO–CO reaction gives PS2.

(v) Region V: $y_{CO} > 0.558$. Finally, we again obtain a poisoned surface PS2 for both the two-component reactions.

The above classification shows that except for the Regions I and V where the two-component systems fall either in PS1 or PS2, the others show two different types of stationary state according to the two-component reactions. In the simulation process we usually start with one of the two-component reactions (i.e., $y_{XO} + y_{CO} = 1$). Keeping y_{CO} fixed we decrease the concentration of the other species in steps of 0.05 (0.01 near the transition) and at the same time add the third species to keep the sum of the total concentration normalised to 1. For each combination of the concentration we start with an empty lattice. The simulation procedure is the same as that applied for two-component NO–CO case.

A hexagonal lattice is generated from a $L \times L$ square lattice as explained earlier (2, 10). In the present work we use $L = 40$ and employ periodic boundary conditions. The simulations are performed on a VAX 11/780 system. The average values of the coverages are taken once we reach the equilibrium state. In the poisoned state the final equilibrium coverages were obtained as an average of 10 independent runs starting with a different random number seed. In the SRS only one run was considered. After discarding the initial 1000 MC cycles (time for the system to achieve the equilibrium) readings were taken after every 10 MC cycles. The coverages and production rates were taken as an average of 400 such readings. The final stationary state depends on the combination of the three species and is discussed below. The CPU time for 10,000 MC cycles is 2 h.

3. RESULTS AND DISCUSSION

3.1. Region I: $y_{CO} < 0.185$

In this region, no matter what the ratio of the concentration of the gases in the reservoir, the lattice is always poisoned by a combination of O and N atoms, except for the pure two-component CO–O_2 reaction where the

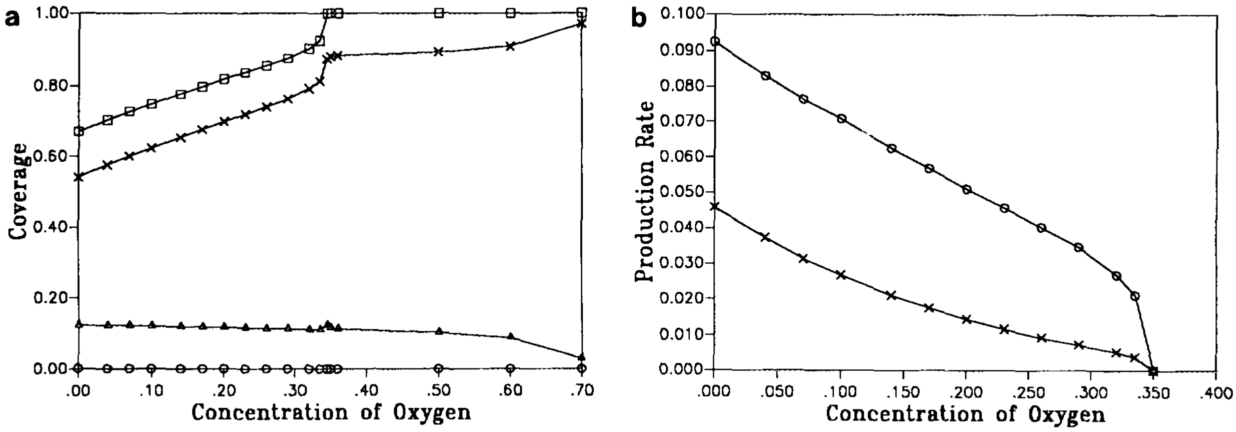

FIG. 1. (a) Plot of surface reactant coverages (θ) versus the oxygen concentration (y_O) at y_{CO} = 0.28. ○, △, ×, and □ represent the coverages of CO, N, O, and the total coverage respectively. (b) Production rates of CO_2 (○) and N_2 (×) as a function of oxygen concentration at y_{CO} = 0.28.

poisoning is by oxygen atoms only. Obviously, since both the two-component reactions give PS1, there is no possibility of a phase transition.

3.2. *Region II: 0.185 < y_{CO} < 0.338*

This region, as already mentioned, is PS1 when $y_{CO} + y_O = 1$ and SRS when $y_{CO} + y_{NO} = 1$. So, for a fixed value of y_{CO} in this region, if we start with $y_{CO} + y_{NO} = 1$ ($y_{CO} + y_O = 1$) and introduce O_2 (NO) at the expense of NO (O_2), we will attain a PS1 (SRS) from a SRS (PS1). This is what we exactly observe through simulation. A typical phase diagram in this region for y_{CO} = 0.28 is shown in Fig. 1a. At y_O = 0., we are in a SRS of the CO–NO two-component reaction. When the concentration of oxygen is slowly increased, the system remains in the SRS until at y_{NO} = 0.381 (y_O = 0.339) it shows a SOPT and goes to PS1. The lattice thereafter is poisoned by a combination of N and O atoms. When NO is gradually replaced by O_2, it is observed that the CO_2 and N_2 production both decrease (Fig. 1b). An increase in O_2 helps in the burn-up of whatever little CO is present on the surface. This further reduces the CO coverage and the sites vacated by CO are preferentially occupied by oxygen atoms. The coverage of oxygen is further enhanced by the direct replacement of NO by O_2. The decrease in NO concentration leads to a lesser production of N_2. However, the coverage of nitrogen remains almost constant with the increase in y_O. This is because in SRS the nitrogen atoms occupy distant sites.

The critical values of y_O (y_{NO}) obtained for different y_{CO}'s fall on a straight line (Fig. 2):

$$y_O = 3.595 y_{CO} - 0.664. \quad [8]$$

3.3. *Region III: 0.338 < y_{CO} < 0.365*

In this region the two-component NO–CO reaction exhibits a PS2, the poisoning being by a combination of N and CO. The CO–O_2 system shows a PS1, the poisoning this time being due only to oxygen atoms. For the three-component system we expect both a FOPT and a SOPT depending upon the relative concentrations of y_{NO} or y_O. We present in detail a typical value of y_{CO} = 0.36 lying in this region. Starting from the pure NO–CO system, as we add oxygen, the system passes from a PS2 to SRS, exhibiting a FOPT at y_O = 0.023. With the further increase of y_O, θ_O increase and θ_{CO} decreases, while θ_N remains almost constant (Fig. 3a), resulting in a decrease in the production of both CO_2 and N_2 (Fig. 3b). This SRS disappears at y_O = 0.635. This is a SOPT and thereafter the system is again in the poisoned state (PS1). In Fig. 2, we have two phase transitions for a given y_{CO} in this region, corresponding to both FOPT and SOPT.

3.4. *Region IV: 0.365 < y_{CO} < 0.558*

For Region IV, we start with the CO–O_2 system and add NO at the expense of oxygen. The system starts from the SRS and exhibits a FOPT to PS2 at a certain critical

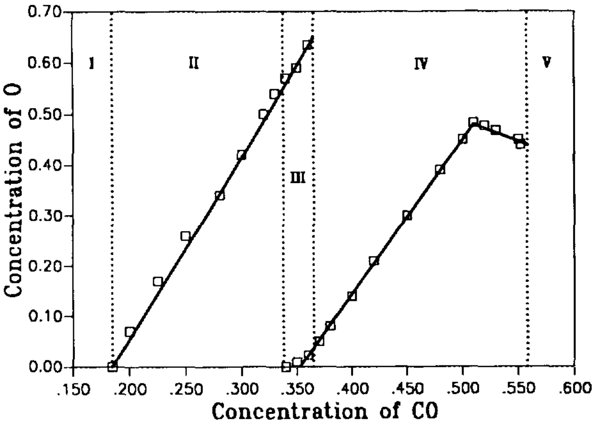

FIG. 2. Loci of second and first order phase transition points in Regions II, III, and IV. The empty squares represent the simulated values and the continuous lines the analytical fits.

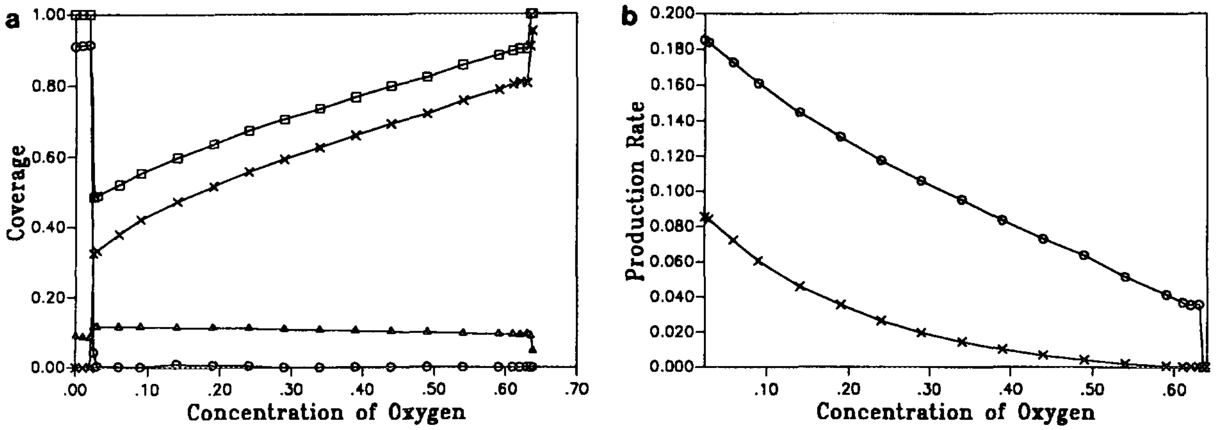

FIG. 3. (a,b) Same as for Figs. 1a,b at $y_{CO} = 0.36$.

value of y_O. The system becomes poisoned by CO and N. With the replacement of O_2 by NO, θ_O decreases, θ_{CO} increases, and θ_N remains almost constant (the reasoning is similar to that for Region II). A typical phase diagram for $y_{CO} = 0.42$ is shown in Fig. 4a. The production of CO_2 and N_2 both increase with the decrease in y_O (Fig. 4b).

The locus of these critical points of y_O plotted versus y_{CO} is again a straight line (Fig. 2), whose equation can be given as

$$y_O = 3.077y_{CO} - 1.087 \quad [9]$$

This linearity breaks down for $y_{CO} > 0.51$. The locus of the points for $0.51 < y_{CO} < 0.558$ is represented by another linear relationship given by

$$y_O = -0.922y_{CO} + 0.956 \quad [10]$$

In the region $0.51 < y_{CO} < 0.558$, even a small amount of NO poisons the system.

To understand this surprising behaviour of the FOPT locus, one has to look into the different coverage rates in CO–O_2 reaction on a hexagonal surface. A detailed study of this reaction on square and hexagonal surfaces has been made previously (8). The coverage θ_{CO} is practically zero for small values of y_{CO}, but as it reaches y_{CO}^{4}, it increases exponentially. For a hexagonal surface it is

$$\theta_{CO} = A\exp(By_{CO}) \quad [11]$$

with $A = 3.691 \times 10^{-10}$ and $B = 33.033$. The coverage of vacant sites is almost linear:

$$\theta_V = 2.50y_{CO} - 0.84 \quad [12]$$

and

$$\theta_O = 1 - \theta_V - \theta_{CO} \quad [13]$$

gives the coverage rate of oxygen. The exponential increase of θ_{CO} and decrease of θ_O becomes noticeable only at about $y_{CO} = 0.51$. In our opinion, this particular change in the coverage rates of CO and O may be the reason for the change of behaviour of the FOPT locus at this particular concentration of CO. This point should be further studied for a better understanding.

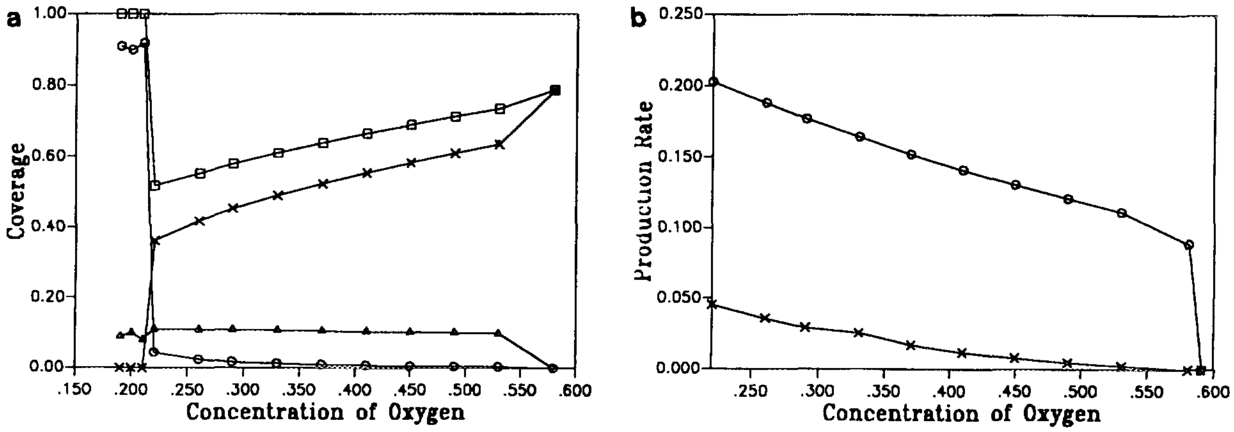

FIG. 4. (a,b) Same as for Figs. 1a,b at $y_{CO} = 0.42$.

3.5. Region V: $y_{CO} > 0.558$

None of the combinations of NO and O_2 give a SRS. The lattice is always poisoned with a combination of CO and N and remains in PS2.

4. CONCLUSIONS

Individual two-component reactions NO–CO and CO–O_2 on a hexagonal lattice have a limited SRS $0.185 < y_{CO} < 0.338$ and $0.365 < y_{CO} < 0.558$, respectively, while in the case of the three-component NO–CO–O_2 reaction we obtain a large region of SRS between $0.185 < y_{CO} < 0.558$ for different combinations of NO and O_2 concentrations. When we consider the window width of the SRS it is obvious that it is enlarged in the case of the three-component reaction. From Figs. 1b, 3b, and 4b it can be observed that the production rate of CO_2 and N_2 decreases as the O concentration increases in the three-component reaction. Conversely, the presence of NO enhances the production rate. Let us consider the case of Fig. 4b. For $y_{CO} = 0.42.$, when $y_O = 0.58$, we are in the two-component regime of the CO–O_2 reaction. We see that in this particular case the production rate of CO_2 is 0.09 whereas that of N_2 is zero. The moment a small amount of NO is added at the expense of O_2 the production rate of CO_2 increases and at the same time N_2 is also produced. As compared to the two-component reaction CO–O_2 the three-component reaction seems to be more favorable for the production of the desorbing gases whenever a SRS exists; on the other hand, it is less favorable when compared to the CO–NO two-component reaction.

In the case of the CO–O_2 reaction the present work shows that when we are close to y^4_{CO} (in SRS), a small addition of NO blocks the catalytic reaction whereas when y_{CO} is close to y^3_{CO}, almost no effect is produced by a small amount of NO. Experimentally (13), it has been observed that a small amount of NO blocks the CO–O_2 reaction on Rh/Al_2O_3 while the reaction is almost unaffected when the catalytic surface is Pt/Al_2O_3. In the present work we have considered the sticking coefficients for the reactants to be 1, but in a previous study (9) we have shown that the real values of the critical points in two-component reactions change according to the relative values of the sticking coefficients of the reactants. Thus, according to our analysis it seems that the reaction CO–O_2 on Rh/Al_2O_3 is taking place near the y^4_{CO} whereas on Pt/Al_2O_3 it occurs near the y^3_{CO}.

From the present MC simulation study, we conclude that a catalytic surface is more efficient to give a steady reactive state in the case of the three-component NO–CO–O_2 reaction than the respective two-component reactions. For the production rate of the desorbing gases it is in an intermediate situation. Moreover, it helps to understand some experimentally obtained results. In view of these interesting observations, the three-component reaction should be further studied by including other refinements in this simple model presented here.

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