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THE EFFECT OF RELATIVE CONCENTRATION OF NO AND O_2 IN A THREE COMPONENT NO-CO-O_2 REACTION FOR THE ELEY-RIDEAL MECHANISM

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Monte Carlo simulations have been used to explore the effect of the Eley-Rideal (ER) mechanism for three component CO-NO-O_2 heterogeneous catalytic reaction on hexagonal lattice. The system is studied for CO and XO; where XO is NO and O_2 with ratio NO:O_2. The effect of ratio NO:O_2 on the catalytic reduction of NO into N and O and oxidation of CO to CO_2 are introduced into the model. Many observations are recorded in this three component reaction. It is observed that with the inclusion of ER mechanism with the Langmuir-Hinshelwood (LH) mechanism, a second order phase transition is eliminated and production of CO_2 and N_2 starts as soon as the CO partial pressure departs from zero. The phase diagrams of the surface coverage with CO, N, O and the steady state production of CO_2 and N_2 are shown as a function of partial pressure of CO in the gas phase.

Keywords: Catalysis, Three-component surface reaction, Monte Carlo simulation, Eley-Rideal mechanism.

1. Introduction

The three-component CO-NO-O_2 catalytic reaction is more complex than two-component CO-NO and CO-O_2 catalytic reaction. These three gases CO, NO and O_2 are present all together in different ratios in automobile exhaust. The conversion of poisonous CO(g) and NO(g) into harmless CO_2(g) and N_2(g) is important to reduce the pollution of atmosphere. This is done by the oxidation of CO with O_2 and reduction of NO with CO on a suitable metal catalyst. Due to the complexity of three-component reaction, not many studies have been carried out for the understanding of surface process, which includes adsorption of reactants, ratio of reactants and surface reaction. The elementary catalytic reactions steps can best be understood by using computational techniques. The technique of Monte Carlo (MC) simulation can be applied for analyzing certain very important aspects of the reaction, under consideration. Ziff, Gulari and Barshad [1] introduced a Monte Carlo simulation technique now popularly known as the ZGB model to study the oxidation of CO by the $2CO + O_2 \rightarrow 2CO_2$ reaction on catalytic surface. In this model a square lattice represents the surface and the reaction occurs via Langmuir-Hinshelwood (LH) mechanism (thermal process). In LH mechanism, both reactants are initially adsorbed on the surface and are in thermal equilibrium with the substrate. The ZGB model exhibits two irreversible phase transitions at y_1(continuous) and y_2(discontinuous). Here y_1 is the critical concentration of CO at which steady reactive state (SRS) starts, while y_2 is the critical concentration of CO where the SRS stops. In this model the transition at $y_1 = 0.389 \pm 0.001$, separates an oxygen poisoned state from SRS, while a transition at $y_2 = 0.525 \pm 0.001$ separates the CO poisoned state from the SRS. To investigate the effect of lattice type on the reaction, Meakin and Scalapino [2] examined the behaviour of the ZGB model of CO – O_2 reaction on a hexagonal lattice (each site has six nearest neighbours (nn)). They found $y_1 = 0.360 \pm 0.005$ and $y_2 = 0.51 \pm 0.001$ for the same reaction on hexagonal surface.

Yaldram and Khan [3, 4] applied the ZGB model to study the CO-NO reaction on square and hexagonal lattice. The importance of the type of lattice for CO-NO reaction system was one of the obvious conclusions of their work. They found that simple LH mechanism does not produce SRS, while SRS exists for hexagonal lattice. They found that the second order phase transition (SOPT) takes place at $y_1 = 0.185$ (±0.002) and first order phase transition (FOPT) takes place at $y_2 = 0.338$ (±0.002).

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Yaldram and Khan [3, 4] used the simple LH mechanism for CO-NO reaction. This simple LH mechanism has been used by number of authors to study the different aspects of this reaction system [5-9]. It has been emphasized by many authors that non-thermal processes are also important to understand the catalytic reactions [10-14]. These processes include the Eley-Rideal (ER) mechanism (a direct reaction between a gas phase atom and an adsorbed atom) and the precursor mechanism of the surface reactions. Where, the precursor mechanism involve direct collisions between chemisorbed species and molecules or atoms that are trapped in the neighbourhood of the surface but have not been thermalized. Meakin [15] has also explored the effect of ER process on the simple ZGB model for the catalytic oxidation of CO by oxygen. Following the ZGB model, several attempts have been made to study different aspects of the CO-NO catalytic reaction system [16-18]. However, relatively less attention has been paid to study the three-component CO-NO-O_2 heterogeneous catalytic reaction through computer simulation.

Yaldram and Khan [19] presented a model for the three-component CO-NO-O_2 reaction on a hexagonal surface. They concluded that the catalytic surface is more efficient in giving a larger SRS in the three-component CO-NO-O_2 reaction than in the respective two-component CO-NO and CO-O_2 reaction. Waqar and Albano [20] presented a model for the three-component reaction on square surface. They showed that the system became YK model when the concentration of oxygen was zero, while it became ZGB model when the concentration of NO was zero. They also showed that with the addition of NO in CO-O_2 reaction, the critical points shifted towards lower values of CO partial pressure, whereas the addition of O_2 in the CO-NO reaction shifted the critical points towards higher values of CO partial pressure. Basit and Waqar [21] showed that with the addition of ER mechanism, position of critical points were not the same as seen in the LH mechanism for square surface.

The main objective of this manuscript is to explore the effects of variation of NO and O_2 concentration alongwith ER mechanism on the phase diagram of the LH model for the three-component CO-NO-O_2 catalytic reaction on hexagonal lattice through Monte Carlo Simulation. In the next section (2), the reaction scheme of the system and simulation procedure is outlined. Results are presented and discussed in Section 3. Finally, the conclusions are presented in Section 4.

2. Model and Simulation

According to LH mechanism, it is assumed that the CO-NO-O_2 reaction occurs according to the following steps :

$$CO(g) + S \rightarrow CO^S \tag{1}$$

$$NO(g) + 2S \rightarrow N^S + O^S \tag{2}$$

$$N^S + N^S \rightarrow N_2(g) + 2S \tag{3}$$

$$O_2(g) + 2S \rightarrow 2O^S$$

$$CO^S + O^S \rightarrow CO_2(g) + 2S \tag{4}$$

Whenever Eley-Rideal mechanism is taken into the consideration then following step is included in simulation model.

$$CO(g) + O^S \rightarrow CO_2 + S \tag{5}$$

Here (g) refers to the gas phase, S is an empty surface site and X^S represents the chemisorbed X-species on the surface. We consider an infinite reservoir filled with CO, NO and O_2 gas molecules with partial pressures (concentrations) y_{CO}, y_{NO} and y_{O2} respectively. The ratio (NO:O_2) is kept fixed, while the ratio of third component (CO) is varied relative to the sum of other two in such a way that $y_{CO} + y_{NO} + y_{O2} = 1$. As such the reaction of CO with the mixture of NO and O_2 is taken with all concentration of y_{CO} from 0 to 1.0 The reservoir is in contact with the surface which is simulated by means of a hexagonal lattice of linear dimension L = 64. It has been shown that an increase in lattice size does not affect the overall qualitative feature of the phase diagram; it slightly changes the critical values [22]. Periodic boundary conditions are applied in order to avoid the boundary effects. The simulation starts with a clean surface and proceeds as follows:

A trial begins with random collision of a gas molecule of one of the reactants with probability y_{CO} or $1 - y_{NO} - y_{O2}$ on the surface of hexagonal lattice. A surface site is chosen randomly and for this chosen site there are two possibilities, i.e, the site is either empty or occupied. For randomly selected site, one of the following events may occur :

a. If the selected site is empty and CO happens to be selected, then CO is adsorbed on the surface as (CO^S) via step (1). Six nearest neighbouring (nn) sites of the adsorbed CO molecule are scanned randomly for the presence of O^S. If any one of the nn sites is occupied by O^S then the reaction step (4) takes place with the creation of two vacant sites on the surface.

b. If CO happens to be selected and the randomly selected site is already occupied by CO^S or N^S, then trial ends. If the selected site is occupied by an O^S atom, then the CO (g) molecule in gas phase directly reacts with O^S with some probability P_{ER} in order to complete the ER step (5). In this case only one site gets vacated.

c. If NO happens to be selected and the randomly selected site is already occupied, then trial ends. On the other hand, if the randomly selected site is empty and NO happens to be selected, then one of nearest neighbouring sites of the vacant site is selected randomly. If the site is occupied, then the trial ends; otherwise NO is dissociated and adsorbed on to these two empty sites via reaction step (2). The dissociation rate of NO into N and O are taken to be 100%. The choice for adsorption on these two sites for N and O is made randomly. Once N and O are adsorbed, the nearest neighbours of each are scanned for the presence of N^S or CO^S in order to complete reaction steps (3) and (4) respectively. If N^S is surrounded by more than one N^S, the one pair of N^S-N^S is selected randomly to give N_2(g) and two sites are vacated. Similarly one pair of CO^S-O^S or CO(g)-O^S is selected randomly to give CO_2(g).

d. If O_2 happens to be selected and if the randomly selected site is occupied, then the trial ends. In case the randomly selected site is vacant, then another vacant site is required to adsorb the O_2 molecule in atomic form. If it finds the second vacant site from the six nn site, then O_2 molecule dissociates into two O atoms which are adsorbed on the surface. After adsorption, the nn sites of these two O^S atoms are scanned for the presence of CO^S to complete the reaction step (4). If two or more pairs of CO^S-O^S exist, then reaction will take place by random selection of one pair of CO^S-O^S. If reaction does not take place between CO^S-O^S, then O^s will reside on the surface and the next MC cycle starts again.

The simulations are carried out on Pentium 4 - PC. The step length for y_{CO} is taken as 0.05, except close to the transition points. In Tables 1 &2, the step length close to the transition points y_1 and y_2, are taken as 0.001 for precise determination of transition points. However, with the inclusion of ER step probability, the step size close to the transition points y_1, is taken as 0.005, whereas the step size of 0.001 is taken close to the transition point y_2. The equilibrium coverages are measured as a function y_{CO}. To locate the critical points, ten independent, runs each up to 50000 Monte Carlo (MC) cycles, are carried out. One MC cycle is equal to L × L trials. If all the ten runs proceed up to 50000 cycles without the lattice becoming poisoned (fully occupied), the particular point is considered to be within SRS. The poisoning of even a single run is a sufficient criterion for considering the point to be in the poisoned state. If the run does not end up in a poisoned state, then in order to get the coverages in SRS, the initial 10000 MC are disregarded and averages are taken over the subsequent 40,000 MC cycles. The values of coverages (production rate) are obtained after 10 MC cycles, so that the final coverage (production) is an average taken over 4000 configurations.

3. Results and Discussions

The earlier work for $CO-O_2$ [2] and CO-NO [3, 4] reactions on hexagonal lattice using LH mechanism is well known. The values of transition points, y_1 and y_2 for $CO-O_2$ reaction are 0.360 ±0.005 and 0.51 ±0.001 respectively. Whereas the values of transition points y_1 and y_2 for CO-NO reaction are 0.185 ±0.002 and 0.338 ±0.001 respectively. In this manuscript the LH mechanism is combined with ER mechanism. Here we have investigated the effect of concentration of ratio of NO:O_2 in the three-component CO-NO-O_2 reaction. In the LH mechanism, for zero concentration of NO, three-component CO-NO-O_2 system behaves like $CO-O_2$ reaction, while for zero concentration of O_2, three-component CO-NO-O_2 system behaves like CO-NO reaction. It confirms the findings of Waqar [20] and Basit[21]. Table 1 shows the transition points and the window width versus NO:O_2 in the mixture according to LH mechanism. In the first row of this table, when the concentration of the both NO and O_2 are equal, the production of CO_2 and N_2 starts at $y_{CO} \approx 0.28$. Here system enters SRS which is consistent with the work of Yaldram and Khan [19]. Table 1 shows the transition points and window width versus NO:O_2 in the mixture in the LH mechanism.

Table1. (Reaction steps 1-4) when the concentration of O_2 is increased and concentration of NO is fixed in LH mechanism.

Ratio NO : O_2	y_1 ±0.001	y_2 ±0.001	MPR of CO_2	MPR of N_2	Window Width
1 1	0.283	0.436	0.196	0.0327	0.153
1 2	0.315	0.460	0.206	0.0206	0.145
1 3	0.330	0.472	0.210	0.0150	0.142
1 4	0.334	0.478	0.211	0.0117	0.144
1 5	0.341	0.483	0.213	0.0097	0.142
1 6	0.344	0.486	0.214	0.0082	0.142
1 7	0.346	0.488	0.214	0.0072	0.142
1 8	0.349	0.490	0.215	0.0063	0.141
1 9	0.353	0.492	0.216	0.0057	0.139

It is observed that in the LH mechanism, with the increase of O_2 concentration in the three-component CO-NO-O_2 reaction, the transition points, y_1 and y_2 are shifted towards higher concentration of CO. Consequently the window width decreases. Moreover, as the concentration of O_2 increases, the maximum production rate of CO_2 increases slowly. Simultaneously production rate of N_2 slowly decreases (Table 1). With the increase of O_2 in NO:O_2 (relatively decreasing the concentration of NO in the mixture) leads to lesser production of N_2. It confirms the findings of Yaldram and Khan [19]. The trends of y_2, the window width (ww) and maximum production rate versus NO/O_2 are shown in Fig.1. Table 2 shows the transition points and the window width versus NO:O_2 in the mixture according to LH mechanism.

Moreover, it is noted from Table 2, that with the increase of NO concentration in the three-component CO-NO-O_2 reaction, the transition points, y_1 and y_2 move towards lower concentration of CO, for the case of LH mechanism. Simultaneously the window width increases slightly. Table 2 indicates that as the relative concentration of NO in the mixture increases, the production of CO_2 decreases. It is consistent with the findings of Grahm et al. [23], while production rate of N_2 slowly increases. Moreover, for zero concentration of O_2 in the mixture, the first transition occurs at y_1 = 0.186, while the second transition occurs at y_2 = 0.339. It confirms YK model [3].

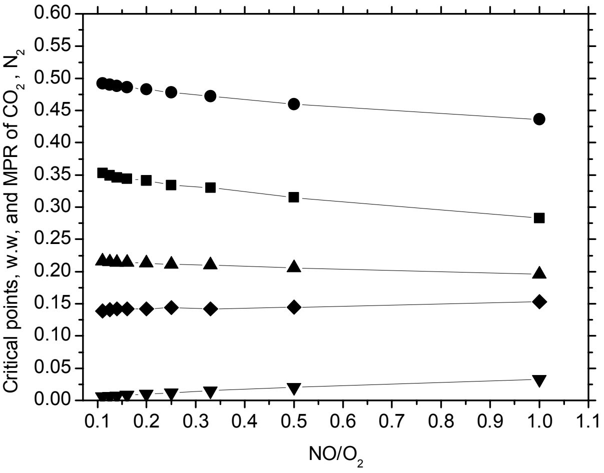

Figure 1. Trends of critical points y_2(solid circle), y_1 (solid square), window width(solid diamond), MPR of CO_2 (solid up triangle), N_2 (solid down triangle) versus NO/O_2 in LH mechanism.

Table 2. (Reaction steps 1-4) when the concentration of NO is increased and concentration of O_2 is fixed in LH mechanism.

Ratio NO : O_2	y_1 ±0.001	y_2 ±0.001	MPR of CO_2	MPR of N_2	Window Width
1 1	0.283	0.436	0.196	0.0327	0.153
2 1	0.252	0.407	0.188	0.043	0.155
3 1	0.234	0.393	0.184	0.051	0.159
4 1	0.224	0.382	0.179	0.057	0.158
5 1	0.218	0.376	0.176	0.067	0.158
6 1	0.210	0.371	0.171	0.067	0.161
7 1	0.205	0.369	0.171	0.068	0.164
8 1	0.202	0.365	0.170	0.068	0.163
9 1	0.200	0.363	0.168	0.069	0.163

In order to understand the effect of NO:O_2 on LH mechanism alongwith ER mechanism on hexagonal lattice for three component CO-NO-O_2 reaction, we have considered three cases with varying y_{CO}:

i. When the concentration of NO = concentration of O_2
ii. When the concentration of NO < concentration of O_2
iii. When the concentration of NO > concentration of O_2

Case (i) for NO = O_2

Fig. 2 shows the phase diagram of the surface coverage and production rate of CO_2 and N_2 for case (i) when ER-step probability P_{ER} of 0.1 is introduced with LH model. It shows that for $y_{CO} = 0$, 83% of the surface is covered with oxygen, 10% of the surface is covered with nitrogen and the other 7% isolated vacancies are randomly distributed on the surface. With the addition of a very small amount of CO ($y_{CO} = 0.005$) and ER-step probability of 0.1, the system enters the SRS with continuous production of CO_2 and N_2. This is because at $y_{CO} = 0.005$, the surface is covered with about 83% of oxygen atoms and therefore ER-mechanism becomes effective and fast in this region with high coverage of adsorbed oxygen and this observation is consistent with the experimental observations [24,25]. Initially, to locate the first transition point y_1, the lowest value of y_{CO} considered in the simulation was $y_{CO} = 0.005$. At this value the system enters the SRS. We therefore assume that the reactive state starts immediately for a non-zero value of y_{CO}. Since with the inclusion of a very small amount of CO ($y_{CO} = 0.005$), the production of CO_2 and N_2 starts, we therefore, conclude that this fact leads to the elimination of y_1 (SOPT). With further increasing the concentration of CO, the production of CO_2 and N_2 increases till the first order phase transition (FOPT) stops the catalytic activity at $y_{CO} = 0.427$ (±0.001) and the surface is poisoned with a combination of CO and N. At $y_{CO} = 0.427$ (±0.001), the coverage of CO on the surface increases suddenly and jumps to a large value (≈ 0.878). For $y_{CO}<y_2$, the coverage of N on the surface decreases more slowly than the coverage for $y_{CO}>y_2$.

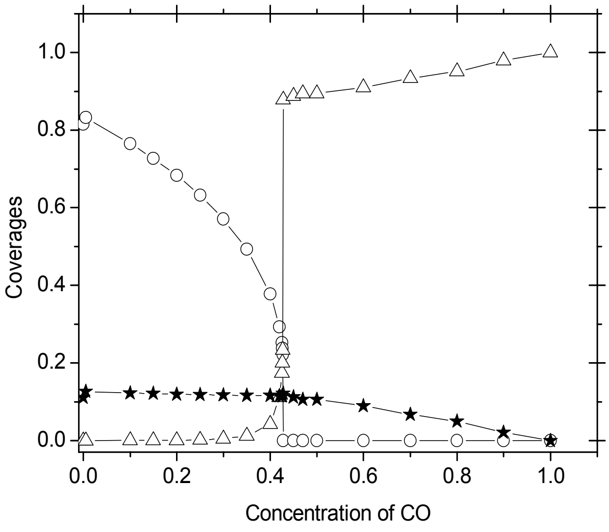

Figure 2a Phase diagram with coverages of surface oxygen (open circles), CO (open triangles), N (stars) for NO:O_2 = 1:1 and ER step probability of 0.1.

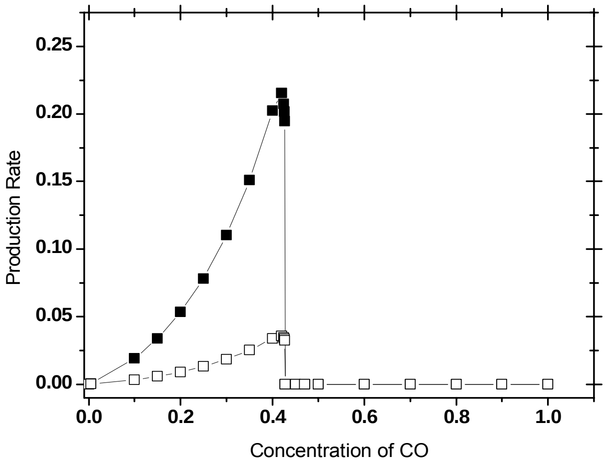

Figure 2b. Production of CO_2 (closed squares) and N_2 (open squares) for NO:O_2 = 1:1 and ER step probability of 0.1.

Case (ii) for NO<O_2:

As we increase the concentration of oxygen in the mixture of NO and O_2 in the ratio of NO:O_2 from 1:1 to 1:9, the transition points y_2 move from 0.427 to 0.484 (Table 3). The results presented in Tabular form (Table 3) are again presented graphically in Fig. 3. These results indicate that the width of reactive region increases with the increase of O_2 concentration in the mixture of reactants.

Table 3. (Reaction steps 1-5) when the concentration of O_2 is increased and concentration of NO is fixed in (NO : O_2), when ER-step probability P_{ER} = 0.1.

Ratio NO : O_2	y_1	y_2 ±0.001	MPR of CO_2	MPR of N_2
1 1	0.0	0.427	0.221	0.037
1 2	0.0	0.455	0.227	0.023
1 3	0.0	0.468	0.239	0.019
1 4	0.0	0.474	0.241	0.016
1 5	0.0	0.478	0.242	0.012
1 6	0.0	0.481	0.243	0.010
1 7	0.0	0.483	0.244	0.008
1 8	0.0	0.485	0.245	0.009
1 9	0.0	0.486	0.259	0.006

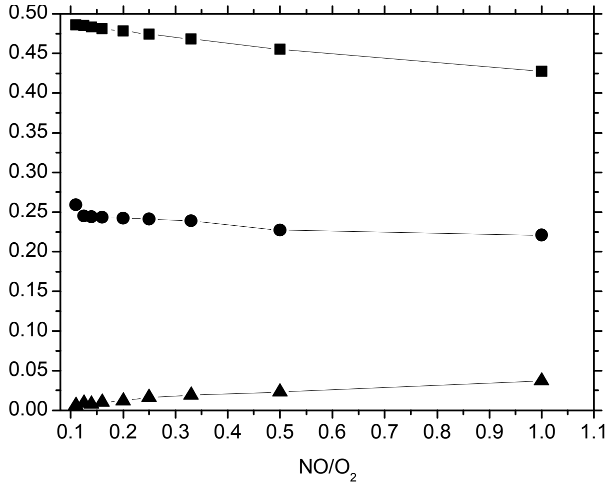

Figure 3. Trend of y_2 (solid square) and production of CO_2 (solid circle) & N_2 (solid up triangle) versus NO/O_2 with ER step probability of 0.1.

It can be seen that with the increase of O_2 concentration, y_2 shifts towards higher concentration of CO.

Fig. 4 shows the phase diagram of the surface coverage and production rate of CO_2 and N_2 when the ratio for $NO:O_2$ is of 1:9. It is also observed that with the increase of concentration of O_2 in the mixture, the maximum production rate (MPR) of CO_2 increases whereas production of N_2 decreases and these observations are shown in Table 3. The rise of production rate of CO_2 can be explained on the basis that enough oxygen becomes available to yield CO_2 production. Therefore for a better catalyst, some mechanism should be developed in exhaust chamber to supply sufficient amount of oxygen to ensure the consumption of oxygen and NO before escaping into the atmosphere.

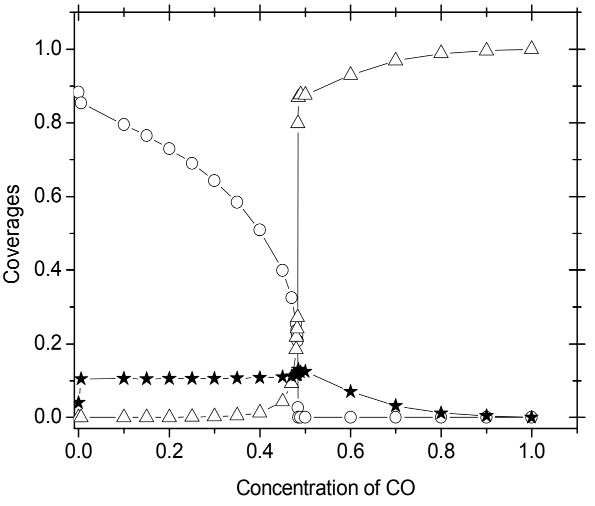

Figure 4a. The same as in Fig.2 (a) but for $NO:O_2$ = 1:9 and ER step probability of 0.1.

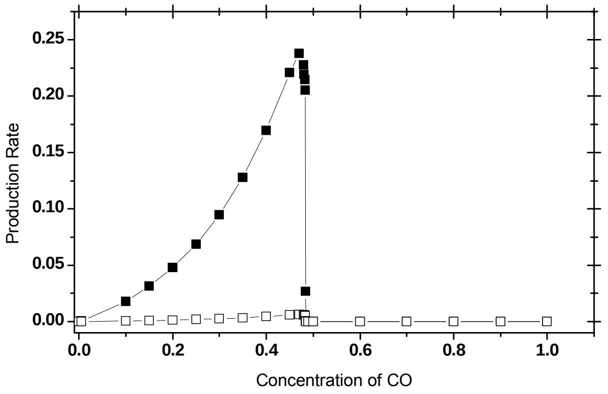

Figure 4b. The same as in Fig. 2(b) but for $NO:O_2$ = 1:9 and ER step probability of 0.1.

Case (iii) for $NO>O_2$:

Table 4. (Reaction steps 1-5) when the concentration of O_2 is fixed and concentration of NO is increased in ($NO : O_2$), when ER-step probability P_{ER} = 0.1.

Ratio NO : O_2	y_1	y_2 ±0.001	MPR of CO_2	MPR of N_2
1 1	0.0	0.427	0.221	0.037
2 1	0.0	0.402	0.209	0.052
3 1	0.0	0.387	0.202	0.061
4 1	0.0	0.376	0.198	0.065
5 1	0.0	0.370	0.194	0.069
6 1	0.0	0.368	0.192	0.072
7 1	0.0	0.362	0.190	0.074
8 1	0.0	0.360	0.189	0.076
9 1	0.0	0.357	0.188	0.077

It can be seen in Table 4 that maximum production of CO_2 decreases continuously with the increase of concentration of NO in the mixture which confirms the findings of Grahm et al.[23]. It is noted that by increasing NO concentration, the production of N_2 also increases. This is due to the dissociation of NO into N and O and hence the coverage of surface with nitrogen increases with the increase of NO concentration (Fig.5 (a)). After, dissociation, these nitrogen atoms are adsorbed on the surface and CO^S molecule is blocked by these atoms. As such, CO^S cannot find O^S on the surface to yield CO_2 gas. Therefore, the width of the reactive region decreases with increase in NO concentration in the mixture. It is also noted that when we increase the concentration of NO in the mixture of NO and O_2 in the ratio of NO:O_2 from 1:1 to 9:1, the coverage of nitrogen becomes higher, while coverage of oxygen becomes lower (Fig. 6). Moreover, with the increase of concentration of NO in the mixture, the transition point y_2 is shifted towards lower concentration of CO (Table 4).

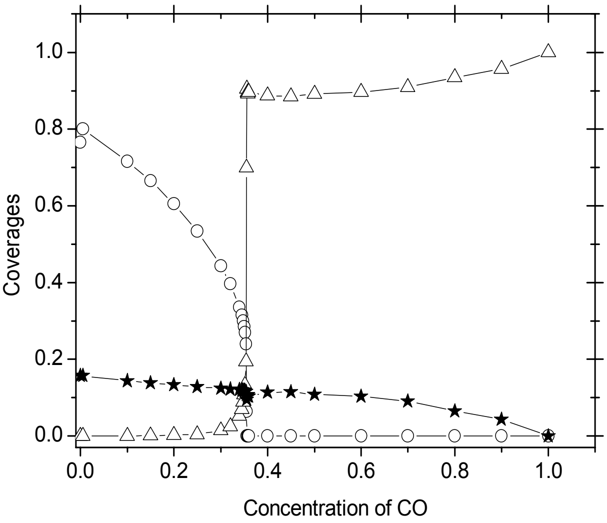

Figure 5a. The same as in Fig.2 (a) but for NO:O_2 = 9:1 and ER step probability of 0.1.

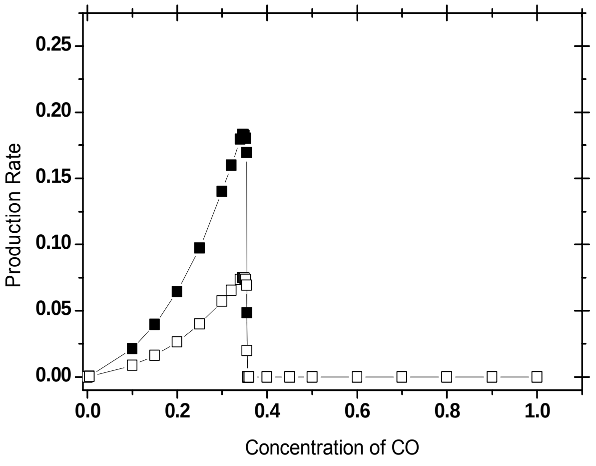

Figure 5b. The same as in Fig. 2(b) but for NO:O_2 of 9:1 and ER step probability of 0.1.

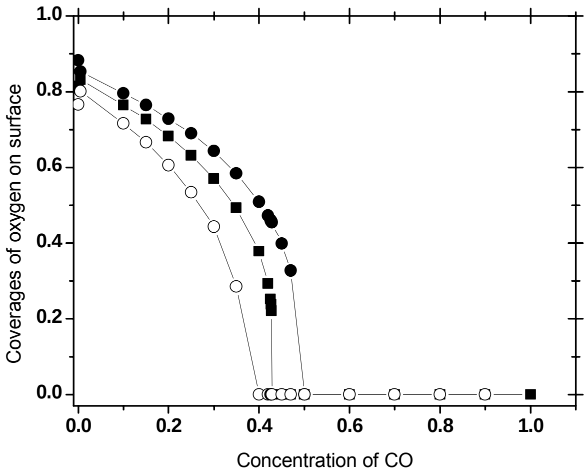

Figure 6. Coverages of surface oxygen vs CO Concentration for NO:O_2 = 1:1 (closed squares); 1:9 (closed circles) and 9:1 (open circles) with ER step probability of 0.1.

4. Conclusion

Yaldram and Khan [19] studied the three components, CO-NO-O_2 as well as the individual two component reactions NO-CO and CO-O_2 on hexagonal lattice. They recorded SRS $0.185<y_{CO}<0.338$ and $0.365<y_{CO}<0.585$ for NO-CO and CO-O_2 reactions respectively. They also have shown that a large SRS exists between $0.185<y_{CO}<0.585$ for purely three-component CO-NO-O_2 reaction with different combinations of NO and O_2 concentration in the mixture. In this regard they recorded the window width as ≈ 0.430 for the three component system. On the other hand, we have carried out a detailed study of ER mechanism for the three-component system CO-NO-O_2 on the hexagonal lattice by varying the concentration of its constituents by Monte Carlo simulation. The ER mechanism in which a reactant (CO) in gas phase directly picks up O^S (atom) from the surface and forms the product CO_2 , adds some interesting features in the phase diagrams of three-component system CO-NO-O_2 that were not seen by considering LH mechanism in YK model [19]. With the introduction of ER mechanism with LH mechanism, a second order phase transition is eliminated and production of CO_2 and N_2 starts the moment $y_{CO} \neq 0$. In YK model [19], the SOPT exits, whereas our model eliminates the SOPT due to the addition of ER mechanism on a simple LH model for the CO-NO-O_2 catalytic reaction on a hexagonal lattice. Moreover, we get the width of reactive region (window width) as ≈ 0.486 for this three component system when the ratio for $NO:O_2$ is 1:9 with ER-step probability $P_{ER} = 0.1$. We hope that this study will contribute in the understanding of three component reaction in real system.

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