The Nucleus **49**, No. 4 (2012) 247-253

The Nucleus
A Quarterly Scientific Journal of Pakistan
Atomic Energy Commission
NCLEAM, ISSN 0029-5698

THE EFFECT OF NO AND O_2 CONCENTRATION IN A THREE COMPONENT CO-NO-O_2 REACTION ON CATALYTIC SURFACE APPLYING THE PRECURSOR MECHANISM: A COMPUTER SIMULATION STUDY

*A.U. QAISRANI and M. KHALID

Department of Physics, Gomal University, Dera Ismail Khan, Pakistan

(Received August 01, 2012 and accepted in revised form December 03, 2012)

We have studied a model for the three component CO-NO-O_2 catalytic reaction on hexagonal surface through Monte Carlo simulations. This study is based on non-thermal process, which involves the precursor motion of CO molecule. 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. Many observations are recorded in the three component reaction. It is observed that with the inclusion of precursor mechanism with the Langmuir-Hinshelwood (LH) mechanism, the reactive window gets enhanced. 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, Precursor mechanism.

1. Introduction

The study of catalytic reaction through computer simulation has now become an active field of research in catalysis. In this field, the three-component CO-NO-O_2 catalytic reaction is more complex than two-component CO-NO and CO-O_2 catalytic reactions. These 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. Many models based on Monte Carlro simulation have been proposed to understand the basics of catalytic surface reactions. Ziff, Gulari and Barshad [1] introduced a Monte Carlo simulation model 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 models the surface and the reaction occurs via Langmuir-Hinshelwood (LH) mechanism (thermal process), in which both reactants are initially adsorbed on the surface and are in thermal equilibrium with the substrate. The ZGB model exhibits two irreversible phase transitions, which separate a steady reactive state (SRS) from surface saturated or poisoned state. A second-order phase transition (SOPT) at $y_1 = 0.389 \pm 0.001$ separates an oxygen poisoned state from SRS, while a first-order phase transition (FOPT) at $y_2 = 0.525 \pm 0.001$ separates the CO poisoned state from the SRS. 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. The transition at $y_1 = 0.389 \pm 0.001$ is continuous, while a transition at $y_2 = 0.525 \pm 0.001$ is discontinuous. However, the second order phase transition has never been observed experimentally in the CO oxidation. The experiments show that production of CO_2 starts as soon CO concentration departs from zero [2, 3]. To investigate the effect of lattice type on the reaction, Meakin and Scalapino [4] examined the behaviour of the ZGB model of CO – O_2 reaction on a hexagonal lattice (each site having six nearest neighbours (nn)). They found $y_1 = 0.360 \pm 0.005$ and $y_2 = 0.510 \pm 0.001$ for the same reaction (CO – O_2) on hexagonal surface.

Yaldram and Khan [5, 6] applied the ZGB model for CO-NO reaction on square as well as hexagonal lattices. The importance of the type of lattice for CO-NO reaction system was one of the obvious conclusions of their work. They found that

---

* Corresponding author : au.qaisrani52@yahoo.com

simple LH mechanism does not produce SRS in a square lattice, 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) for the hexagonal lattice.

Yaldram and Khan [5, 6] used the simple LH mechanism for CO-NO reaction. This simple LH mechanism has been used by number of authors to study the different aspect of this reaction system [7-11]. It has been emphasized by many authors that non-thermal processes are also important to understand the catalytic reactions [12-16]. One of such processes includes the precursor mechanism. In this mechanism, a molecule striking the surface does not come to thermal equilibrium with the surface but remains in motion for some period of time. We refer to these trapped particles that are not in thermal equilibrium with surface as, “precursors”. Harris et al. [15] have explained the precursor mechanism in detail. However, relatively less attention has been paid to study the three-component CO-NO-O_2 heterogeneous catalytic reaction through computer simulation.

Yaldram et al. [17] 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 reactions. Ahmad and Albano [18] presented a model for three-component reaction on square surface and 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 Ahmad [19] showed that with the addition of Eley-Rideal mechanism (a direct reaction between a gas phase atom and an adsorbed atom), position of critical points were not the same as seen in the LH mechanism for square surface.

The objective of this manuscript is to explore the effects of precursor 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, 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:

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

$$NO(g) + 2S \rightarrow N^S + O^S \qquad (2)$$

$$O_2(g) + 2S \rightarrow 2O^S \qquad (3)$$

$$N^S + N^S \rightarrow N_2(g) + 2S \qquad (4)$$

$$CO^S + O^S \rightarrow CO_2(g) + 2S \qquad (5)$$

Whenever precursor mechanism is taken into consideration, then following steps are simulated

$$CO(g) + S \rightarrow CO^P + S \qquad (6)$$

$$CO^P + O^S \rightarrow CO_2(g) + S \qquad (7)$$

$$CO^P + S \rightarrow CO^S \qquad (8)$$

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.

We will consider the motion of a precursor upto a maximum distance R from the original point of impact. A specific pattern for the set of sites around the original point of impact is called “environment” of impact R. Therefore, for hexagonal lattice, the first environment consists of six first nearest neighbouring (1nn) sites from the site of impact. The second environment consists of six 1nn sites and six second nearest neighbouring (2nn) sites, whereas the third environment consists of all twelve sites of second environment and additional six third nearest neighbouring (3nn) sites. However, we will consider the mobility of a precursor upto the first-nearest neighborhood (in the first environment).

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. The equilibrium coverages are measured as a function of y_{CO}. In order to locate the critical points, ten independent runs each up to 50,000 Monte Carlo (MC) cycles are performed. If the run does not end up in a poisoned state (surface saturation) and completes 50000 MC cycles, then the system is considered to be within SRS. In order to obtain the coverages corresponding to the SRS, the initial 10,000 MC cycles are disregarded and the averages are taken over the subsequent 40,000 MC cycles. The values of coverages (production rate) are obtained after every 10 MC cycles, so that the final coverage (production rate) is an average taken over 4000 configurations. The reservoir is in contact with the surface which is simulated by means of a hexagonal lattice of linear dimension L = 64. It is observed that increase in the lattice size does not affect the quality of the phase diagram; it slightly increases the critical values [20]. Periodic boundary conditions are applied in order to avoid the boundary effects. The simulation for the 1st environment is carried. 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 there are two possibilities. The CO molecule can either be adsorbed on the empty site through step (1) or it can undergo a precursor mechanism through step (6). The probability of each event is 0.5 i.e. step (1) and step (6) are equally probable. In case the CO molecule is adsorbed on the surface as (CO^S) via step (1), then six nearest neighbouring (nn) sites of the adsorbed CO molecule are scanned randomly for the presence of O^S. If any of the nn sites are occupied by O^S then the reaction step (5) takes place to produce CO_2(g) with the creation of two vacant sites on the surface. The generation of vacant sites on the surface is necessary to maintain catalytic activity in an efficient way. In case the CO molecule is selected to execute the precursor mechanism, a precursor CO^P is produced via step (6). This (CO^P) moves around the first nearest neighbours and if it finds oxygen there, it reacts with adsorbed oxygen atom via reaction step (7). The output of this reaction step is production of CO_2(gas) and creation of one vacancy. If the precursor CO^P does not find oxygen there within the specified range, then it looks for a vacant site (out of six 1nn) and gets adsorbed on any of the vacant sites of the specified range via reaction step (8) and then goes for usual reaction step (5) as mentioned above.

b. If NO happens to be selected and the randomly selected site is already occupied, then the trial ends. 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 these two empty sites via reaction step (2). The dissociation rate of NO into N and O is 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 (4) and (5) respectively. If N^S is surrounded by more than one N^S, then only 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 is selected randomly to give CO_2(g).

c. 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 into two O^S 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 (5). If two or more pairs of CO^S-O^S exit, then reaction will take place by random selection of one pair of CO^S-O^S. If pair of CO^S-O^S does not exist, then O^s will reside on the surface and the next MC cycle starts again.

3. Results and Discussion

The earlier work for CO-O_2 [4] and CO-NO [5, 6] reaction on hexagonal lattice using LH mechanism is well known. In this work, the quoted values of transition points, y_1 and y_2 for CO-O_2 reaction are 0.365 ±0.005 and 0.558 ±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. 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 O_2 (Table 1), three-component CO-NO-O_2 system behaves like CO-NO reaction, while for zero concentration of NO (Table 2), three-component CO-NO-O_2 system behaves like CO-O_2 reaction. This confirms the findings of Ahmad and Albano [18] and Basit and Ahmad [19].

Table1. (Reaction steps 1-5) 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 0	0.185	0.339	0.1584	0.0793	0.154
1 1	0.283	0.436	0.1960	0.0327	0.153
1 2	0.315	0.460	0.2058	0.0202	0.145
1 3	0.330	0.472	0.2070	0.0149	0.142
1 4	0.334	0.478	0.2193	0.0137	0.144
1 5	0.341	0.483	0.2124	0.0129	0.142
1 6	0.344	0.486	0.2236	0.0083	0.142
1 7	0.346	0.488	0.2233	0.0080	0.142
1 8	0.349	0.490	0.2307	0.0075	0.141
1 9	0.353	0.492	0.2316	0.0073	0.139

Table 1 shows the transition points and window width versus NO:O_2 in the mixture for LH mechanism only. It is observed that in 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 toward higher concentration of CO. Consequently window width decreases. Moreover, as the concentration of O_2 increases, the production rate of CO_2 slowly increases, while production rate of N_2 slowly decreases (Table 1). With the increase of concentration of O_2 in NO:O_2 relatively decreasing the concentration of NO in the mixture leads to a lesser production of N_2, which confirms the findings of Yaldram and Khan [17]. Table 2 shows the transition points and the window width versus NO:O_2 in the mixture for a fixed concentration of O_2 while LH mechanism is exercised.

Table 2. (Reaction steps 1-5) when the concentration of NO is increased and concentration of O_2 is fixed in the LH mechanism.

Ratio NO : O_2	y_1 ±0.001	y_2 ±0.001	MPR of CO_2	MPR of N_2	Window Width
0 1	0.366	0.550	0.3001	0.000	0.184
1 1	0.283	0.436	0.196	0.032	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

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 maximum production rate (MPR) of CO_2 decreases which is consistent with the findings of Grahm et al.[21], while production rate of N_2 slowly increases. Moreover, for zero concentration of O_2, the first transition occurs at y_1 = 0.185 ± 0.001, while the second transition occurs at y_2 = 0.339 ± 0.001. It confirms YK model [5].

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

(i) concentration of NO = concentration of $O_{2.}$

(ii) concentration of NO < concentration of $O_{2.}$

(iii) concentration of NO > concentration of $O_{2.}$

Case (i) for NO = O_2

Since in our present model, only a single vacant site is required for CO molecule to be adsorbed on the surface, whereas two nn sites are required for both NO and O_2, due to the precursor motion of CO, the CO^P molecule starts consuming the chemisorbed oxygen atom trapped between N^S-N^S pair leaving behind a vacant site on the surface. This vacant site blocks the further adsorption of NO, as NO needs two vacant sites for its adsorption. Simultaneously there is no chance of adsorption for O_2 on a single vacated site. Therefore, the chance of adsorption for CO on the vacant site increases and consequently indirect supply of CO gas increases and hence the reactive window increases. We conclude that with the inclusion of the precursor mechanism, the critical points are not the same as observed in the LH mechanism. Fig. 1 shows the phase diagram with surface coverage and production rate of CO_2 and N_2 when the ratio for NO:O_2 is 1:1.

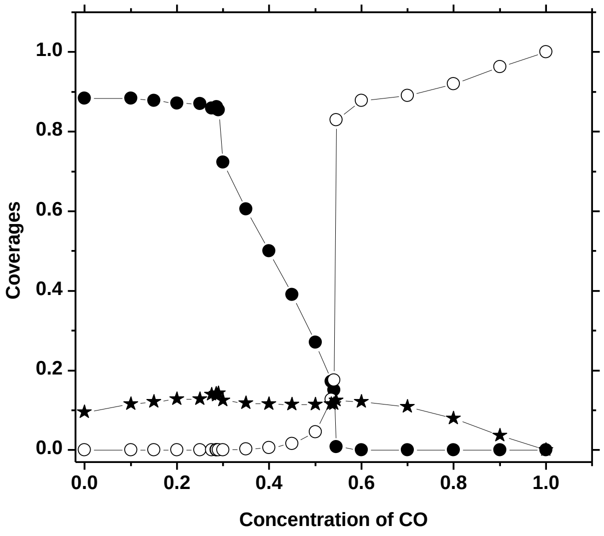

Figure 1a. Phase diagram with coverages of surface oxygen (solid circles), CO (open circles), N (stars) for NO:O_2 = 1:1 with 50% precursor probability.

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 0.545 to 0.605. In other words, with the increase of O_2 concentration, y_2 shifts towards higher concentration of CO.

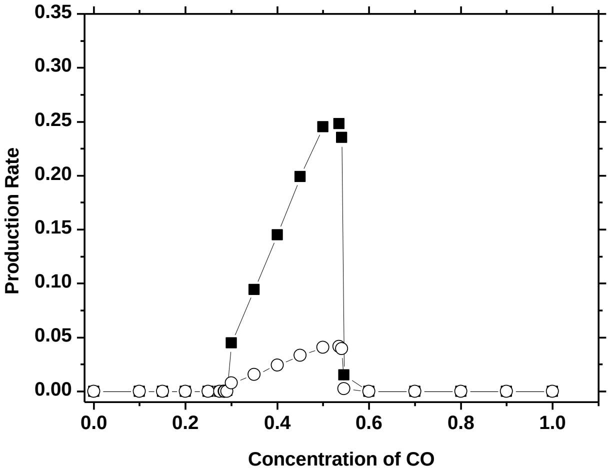

Fig.1 (b). Production of CO_2 (closed squares) and N_2 (open circles) for NO:O_2 = 1:1 with 50% precursor probability.

Fig. 2 shows the surface coverage and production rate of CO_2 and N_2 when NO:O_2 is in the ratio 1:9. It is also observed that with the increase of concentration of O_2 in the mixture, the production of CO_2 increases whereas production of N_2 decreases and these observations are shown in Table 3. The increase of production rate of CO_2 can be explained on the basis that enough oxygen becomes available for CO^P to yield CO_2(g). Therefore, for a better catalyst, some mechanism should be developed in exhaust chamber to supply sufficient amount of oxygen to ensure the consumption of CO and NO before escaping into the atmosphere.

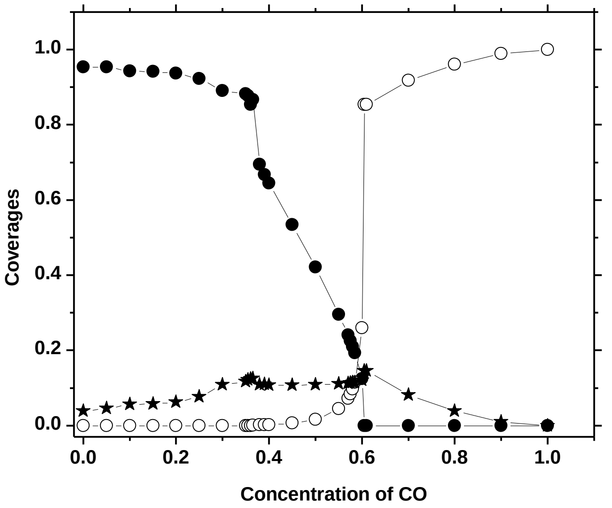

Figure 2a. The same as in Fig.1 (a) but for NO:O_2 = 1:9.

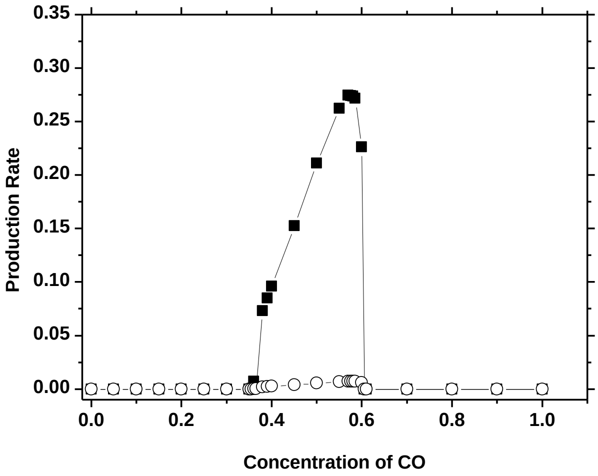

Figure 2b. The same as in Fig.1 (b) but for NO:O_2 = 1:9.

Table 3. (Reaction steps 1-8) when the concentration of O_2 is increased and concentration of NO is fixed in (NO : O_2) along with precursor mechanism.

Ratio NO : O_2	y_1 ±0.005	y_2 ±0.005	MPR of CO_2	MPR of N_2
1 1	0.285	0.545	0.2616	0.0433
1 2	0.320	0.570	0.2714	0.0272
1 3	0.335	0.585	0.2757	0.0197
1 4	0.345	0.590	0.2781	0.0154
1 5	0.345	0.595	0.2795	0.0127
1 6	0.350	0.600	0.2807	0.0108
1 7	0.355	0.600	0.2818	0.0094
1 8	0.355	0.600	0.2823	0.0083
1 9	0.360	0.605	0.2825	0.0074

Table 4. (Reaction steps 1-8) when the concentration of O_2 is fixed and concentration of NO is increased in (NO : O_2) along with precursor mechanism.

Ratio NO : O_2	y_1 ±0.005	y_2 ±0.005	MPR of CO_2	MPR of N_2
1 1	0.285	0.545	0.2616	0.0433
2 1	0.260	0.510	0.2436	0.0610
3 1	0.240	0.495	0.2313	0.0693
4 1	0.235	0.485	0.2310	0.0772
5 1	0.225	0.489	0.2307	0.0824
6 1	0.220	0.475	0.2287	0.0857
7 1	0.215	0.470	0.2258	0.0875
8 1	0.210	0.465	0.2248	0.0904
9 1	0.205	0.460	0.2237	0.0921

Case (iii) for NO>O_2

Table 4 & Fig.4 depict 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. [21], whereas the production of N_2 increases. This is due to the dissociation of NO into N and O and hence the coverage of surface with nitrogen increases (Fig.3). These nitrogen atoms adsorbed on the surface block the surface sites as there is no reaction of N with CO. 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. Moreover, with the increase of concentration of NO in the mixture, the transition point y_1 and y_2 are shifted towards lower concentration of CO (Table 4 & Fig.5).

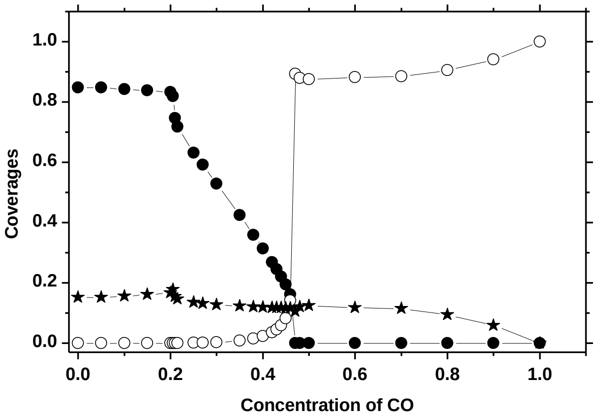

Figure 3a. The same as in Fig.1 (a) but for NO:O_2 = 9:1.

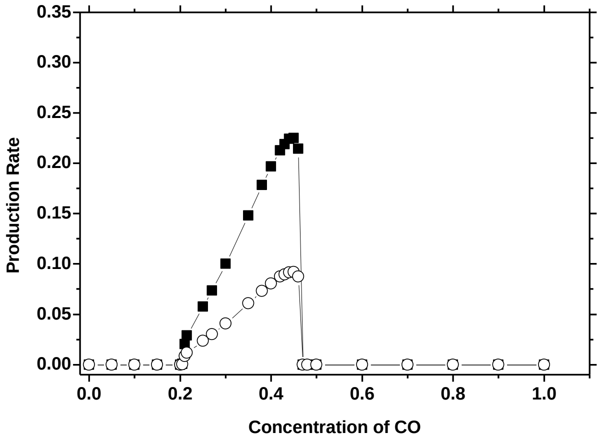

Figure 3b. The same as in Fig.1b but for NO:O_2 = 9:1.

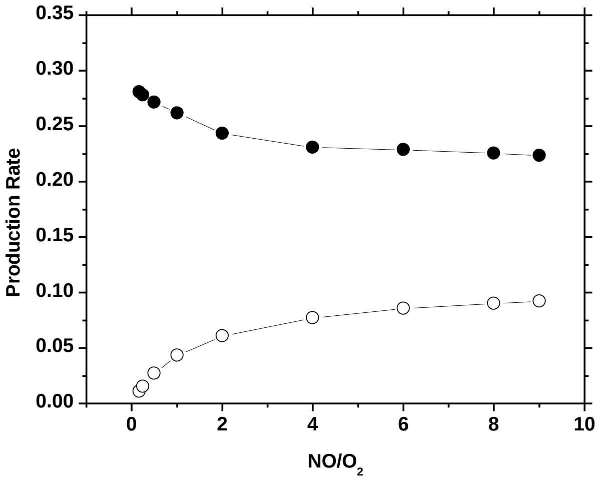

Figure 4. Production rates of CO_2 (closed circles) and N_2 (open circles) versus NO/O_2 for 50% precursor of CO.

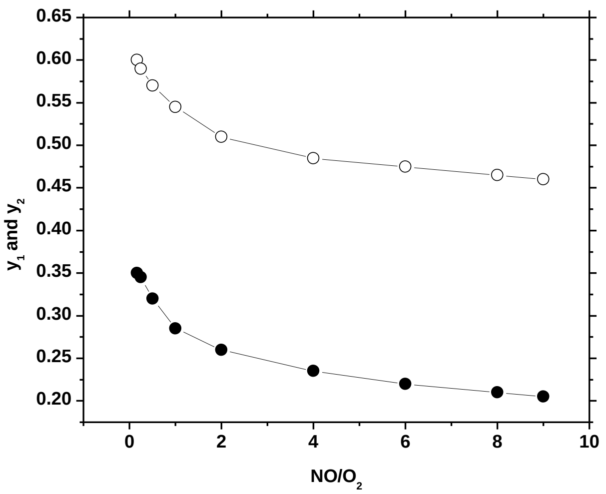

Figure 5. Trends of critical points y_1 (closed circles) and y_2 (open circles) versus NO/O_2 for 50% precursor of CO.

4. Conclusion

We have studied the effect of precursor mechanism on the phase diagram of LH type model for the three-component CO-NO-O_2 catalytic reaction on hexagonal lattice by varying the concentration of its constituents by Monte Carlo simulation. The precursor mechanism adds some interesting features in the phase diagrams of three-component system CO-NO-O_2 on the hexagonal lattice that were not seen by considering LH mechanism. It is concluded that the phenomenon of precursor increases the window width. We hope that this study will contribute to the understanding of three component reaction in real system. In view of these observations, the three-component system CO-NO-O_2 should be studied further by considering precursor motion up to second and third environment.

References

[1] R. M. Ziff, E. Gulari and Y. Barshad, Phys. Rev. Lett. **56** (1986) 2553.

[2] M. Dumont et al., J. Catal. **122** (1990) 95.

[3] F. Bagnoli et al., J. Chem. Phys. **94** (1991) 777.

[4] P. Meakin and D.J. Scalapino, J. Chem. Phys. **87** (1987) 731.

[5] K. Yaldram and M. A. Khan, J. Catal. **131** (1991) 369.

[6] K. Yaldram and M.A. Khan, J. Catal. **136** (1992) 279.

[7] J. Cortes, H. Puschman and E. J. Valencia, Chem.Phys. **109** (1998) 6086.

[8] A.G. Dickman, Phys. Rev. E **59** (1993) 6361.

[9] K. Yaldram, K.M. Khan, N. Ahmad and M.A. Khan, J. Phys A: Math. Gen. **26L** (1993) 805.

[10] B.J. Brosilow and R.M. Ziff, J. Catal.**136** (1992) 275.

[11] B. Meng, W.H. Weinberg and J. W. Evan, Chem. Phys. **101** (1994) 3234.

[12] N.O. Wolf, D.R. Burgess and D.K. Hoffman, Surf. Sci. **100** (1980) 453.

[13] S.P. Sing-Boparai, M. Bowker and D. A. King, Surf. Sci. **53** (1975) 55.

[14] G. Comsa, R. David and B. J. Schumacher, Surf. Sci. **95** (1980) L210.

[15] J. Harris , B. Kasemo and E. Tornqvist, Surf. Sci. **105** (1981) L281.

[16] B. Jackson and M. Person, J. Chem. Phy. **103** (1995) 6257.

[17] K. Yaldram, K.M. Khan, N. Ahmad and M.A. Khan, J. Catal. **147** (1994) 96.

[18] W. Ahmad and E. V. Albano, Appl. Surf. Sci. **254** (2008) 2436.

[19] A. Basit and W. Ahmad, J. Korean. Phys. Soc. **59** (2011) 134.

[20] K.M. Khan, K. Yaldram, N. Ahmed and Q. Haque, Physica A **268** (1999) 89.

[21] G.W. Graham, A. D. Logan and M. Shelef, J. Phys. Chem. **97** (1993) 5445.