

## TRANSIENT NON-THERMAL MOBILITY OF CO FOR CO-NO CATALYTIC REACTION ON HEXAGONAL LATTICE: A COMPUTER SIMULATION STUDY

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Monte Carlo simulation has been used to study the effect of precursor mechanism along with diffusion of N on a hexagonal lattice for CO-NO heterogeneous catalytic reaction. The reactive window gets enhanced due to the precursor mechanism. It has been also found that the diffusion of N slightly shifts the first order transition ( $y_2$ ) toward higher concentration of CO and therefore by including the diffusion of N the reactive window gets wider. It is observed that whenever precursor mechanism is introduced, the production of CO<sub>2</sub> and N<sub>2</sub> starts as soon as the CO partial pressure ( $y_{CO}$ ) departs from zero. The reactive window and production rate increases by increasing the range of precursor mobility.

**Keywords:** Catalysis, Monte Carlo simulation, Precursor mechanism, Nitrogen oxides.

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### 1. Introduction

The study of catalytic surface reaction through computer simulation has now become an active field of research in the field of catalysis. To study the catalytic reaction, some models have been developed. A simple monomer-dimer model to describe the oxidation of carbon monoxide on catalytic surface was introduced by Ziff, Gulari and Barshad [1] as a computer simulation and is known as the ZGB model. The ZGB model is the simplest model to explain the actual process involved in the catalytic oxidation of CO. In this model the reaction occurs via the Langmuir-Hinshelwood (LH) mechanism, in which both the reactants are initially adsorbed on the surface and are in thermal equilibrium with the surface. 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 a 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

at  $y_2 = 0.525 \pm 0.001$  is discontinuous. However, the second order phase transition (SOPT) has never been observed experimentally in the CO oxidation. The experiments show that production of CO<sub>2</sub> starts as soon as CO concentration departs from zero [2,3]. Following the introduction of ZGB model, several attempts have been made in order to give more realistic description of the ZGB model and its variants [4-11]. Together with the oxidation of CO, there has also been interest in the oxidation of CO by NO. The understanding of steps involved in the CO-NO catalytic reaction is complicated. Yaldrum and Khan [12,13] proposed a reaction model based on the ZGB model for the catalytic reaction of CO - NO on square and hexagonal lattice. The reaction model in which NO reacts with CO is based on the LH mechanism. With this simple LH mechanism they have shown that that the square lattice does not support the steady reactive state. However, increasing the coordination number of the lattice two transition points are observed for hexagonal lattice, where each lattice site has six nearest neighbours (nn). The other mechanism called the precursor mechanism, which involves the direct collision between the chemisorbed species and molecules or atoms that are trapped in the neighbourhood of the surface but have not been thermalized is

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explained in detail by Harris and Kasemo [14,15].

Very recently, Khalid and Qaisrani [16-18] have studied the effect of transient non-thermal mobility of CO for CO-NO reaction on square and body-centered cubic lattice. However, the effect of diffusion of N along with precursor mechanism on hexagonal lattice for CO-NO heterogeneous catalytic reaction was not considered in their studies. Therefore it was desirable to investigate the precursor mechanism of CO<sup>P</sup> molecule along with the diffusion of N for CO-NO catalytic reaction on hexagonal lattice.

In this manuscript, we have studied the combined effect of precursor mechanism along with diffusion mechanism of nitrogen for CO-NO catalytic reaction on the hexagonal lattice through Monte Carlo simulation.

## 2. Model and Simulation

According to LH mechanism, it is assumed that the reaction occurs according to the following steps:



Whenever Precursor mechanism is taken into consideration then following steps are simulated



Here (g), and S indicate gas phase and active surface sites respectively; while X<sup>S</sup>, and X<sup>P</sup> represent X adatom on the surface site S and the molecule executing precursor mechanism respectively. We consider a surface in contact with an infinite reservoir filled with CO and NO with partial pressure  $y_{\text{CO}}$  and  $1-y_{\text{CO}}$  respectively. The relative impingement rates of CO and NO on the surface sites are taken to be proportional to their partial pressures respectively in such a way that the total probability is normalized to one.

The equilibrium coverages are measured as a function of  $y_{\text{CO}}$ . 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 catalytic surface is simulated by means of a hexagonal lattice of size  $L=64$ . It is observed that increase in the lattice size does not affect the quality of the phase diagram; it slightly increases the critical values [19]. Periodic boundary conditions are applied in order to avoid the boundary effects. We have considered three different ranges of the surface environment. In the simulation of hexagonal lattice, the first environment consists of six first nearest neighbouring (1nn) sites from 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 6 third nearest neighbouring (3nn) sites. Therefore, the first, second and third environment in the hexagonal lattice consists of 6, 12 and 18 neighbouring sites respectively (Fig. 1). The simulation of these three environments is carried out separately. In this simulation, the following models are studied:

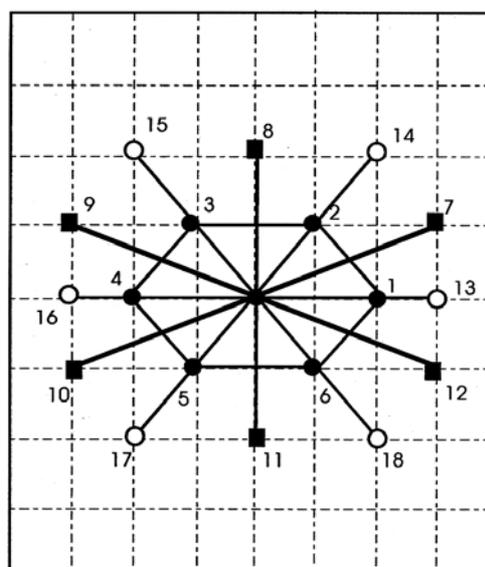


Figure 1. Hexagonal surface where sites marked by 1-6 are at first nn, the sites marked by 7-12 are at second nn and the sites 13-18 are third nn.

*Model A*

In Model A, steps 1-6 are considered. The simulation starts with a clean surface and proceeds as follows: CO or NO is selected with a probability  $y_{\text{CO}}$  or  $1-y_{\text{CO}}$  respectively. A surface site is selected randomly. If the site is occupied the trial ends. If the site is empty and CO is the selected molecule 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 (5). The probability for each event is 0.5 i.e. step (1) and step (5) are equally probable. In case the CO molecule is adsorbed through step (1), then six nearest neighbours are scanned for the presence of an O atom. If an O atom is present then the CO reacts with O through step (4) to produce  $\text{CO}_2(\text{g})$ . This  $\text{CO}_2$  desorbs from the surface leaving behind two vacant sites on the surface. In case the CO molecule is selected to execute the precursor mechanism and consequently a precursor  $\text{CO}^{\text{P}}$  is produced via step (5). This ( $\text{CO}^{\text{P}}$ ) moves around the first nearest neighbours and if it finds oxygen there, it reacts with adsorbed oxygen atom via reaction step (6). The output of this reaction step is production of  $\text{CO}_2(\text{gas})$  and creation of one vacancy. If the precursor  $\text{CO}^{\text{P}}$  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 (1) and then goes for usual reaction step (4) as mentioned above. While for adsorption of NO the reaction step (2) is simulated. After adsorption, N atoms go for reaction step (3). In the first case, N atom scans its first nn for the presence of another N atom. If it finds N atom there, then it reacts with it with the production of  $\text{N}_2(\text{g})$ .  $\text{N}_2(\text{g})$  desorbs immediately leaving behind two vacant sites. In the second case adsorbed O atom reacts with  $\text{CO}^{\text{S}}$  molecule and produces  $\text{CO}_2(\text{g})$  which desorbs immediately leaving behind two vacant sites via reaction step (4). It is worth mentioning here that the reaction probability of a precursor  $\text{CO}^{\text{P}}$  with a chemisorbed oxygen is taken to be maximum (100%) in our simulation. In summary, molecule CO executes precursor motion in the first environment in model A.

*Model B*

For Model B all the simulation steps remain the same as mentioned in model A, but the only difference is in the range of precursor molecule. In

this model CO molecule executes precursor motion up to second environment.

*Model C*

For Model C all the simulation steps remain the same as mentioned in Model A, but range of the mobility of CO molecule (precursor range) gets extended up to third environment.

*Model D*

In this case for model D the simulation procedure remains the same as mentioned for the model A with the introduction of diffusion of adsorbed nitrogen atoms. In the diffusion mechanism when the random selection of site is made for already adsorbed  $\text{N}^{\text{S}}$ , the nearest neighbours of this  $\text{N}^{\text{S}}$  site are scanned randomly. If its nn of adsorbed ( $\text{N}^{\text{S}}$ ) is found empty, then this adsorbed  $\text{N}^{\text{S}}$  is moved to the vacant site. After the diffusion of nitrogen the nearest neighbour of the new position is scanned for the presence of  $\text{N}^{\text{S}}$  via reaction step (3). The output of this step is the production of  $\text{N}_2(\text{g})$  along with the vacation of two sites on the surface.

**3. Results and Discussion**

The earlier attempt to study the mechanism of CO-NO catalytic reaction through computer simulation on the square lattice failed to get steady reactive state by LH mechanism and without diffusion [12]. This was due to the trapping of Nitrogen atom by Oxygen or vice versa and consequently it stopped the production of  $\text{CO}_2(\text{g})$  and  $\text{N}_2(\text{g})$  and hence the square lattice is poisoned by the process of "chequerboarding" of N atoms [20]. The chequerboarding of  $\text{N}^{\text{S}}$  atoms or  $\text{O}^{\text{S}}$  atoms can not take place geometrically on the hexagonal surface. Therefore the SRS window although it was small ( $y_1=0.185$  and  $y_2 = 0.338$ ) in the case of the CO-NO catalytic reaction on hexagonal surface and was reported by Yaldram et al [12,13]. These results [12-13] motivated us to explore the effect of precursor mechanism for CO-NO catalytic reaction on hexagonal lattice.

Since in our present model, only a single vacant site is required for CO molecule to be adsorbed on the surface, whereas NO needs a pair of nn sites. Due to the precursor motion of CO, the  $\text{CO}^{\text{P}}$  molecule starts consuming the chemisorbed oxygen atom trapped between  $\text{N}^{\text{S}}-\text{N}^{\text{S}}$  pair leaving behind a vacant site on the surface. This vacant site blocks the incoming NO to be adsorbed on the

surface, as NO needs two vacant sites for its adsorption. Therefore the chance of adsorption for CO on the vacant site increases and consequently indirect supply of CO gas increases and hence  $y_1$  is shifted towards lower concentration of CO. Considering the precursor mobility in the first environment, the moment  $y_{CO}$  departs from zero, the productive activity starts and the system enters in to an SRS (Fig. 2). The lowest value of  $y_{CO}$  considered in the simulation was  $y_{CO} = 0.001$ . At this value the equilibrium state of the system was the steady reactive state. We therefore assume that the reactive state starts immediately for a non zero value of  $y_{CO}$ . The steady reactive state of width 0.303 is observed in our simulation when the precursor mechanism is introduced in the first environment. The transitions points  $y_1$  and  $y_2$

corresponding to the three different ranges of the surface environment are given in the Table1. It is important to note that the usual SOPT disappears.

Table 1. Transition points/window width and MPR vs range of precursor on hexagonal lattice

Range of Precursor	$Y_1$	$Y_2$	Window width	MPR
1nn	0.0	$0.303 \pm 0.001$	$0.303 \pm 0.001$	0.2518
2nn	0.0	$0.388 \pm 0.001$	$0.388 \pm 0.001$	0.3538
3nn	0.0	$0.416 \pm 0.001$	$0.416 \pm 0.001$	0.3920

It is evident from Fig. 2 that in the case of the first environment, the window width is larger than that of the window width observed in LH mechanism. [12,13]. It has been also found and shown in Fig. 3 that width of reactive region ( $w$ ) increases if the movement of precursor is extended to 2<sup>nd</sup> nn and 3<sup>rd</sup> nn. The steady reactive state (SRS) for each reaction model is studied in our simulation and it is observed in our simulation that maximum production rate (MPR) of  $CO_2(g)$  and  $N_2(g)$ , both increases with the range of precursor mobility. The MPR of  $CO_2(g)$  versus the range of precursor mobility is shown in Fig. 4.

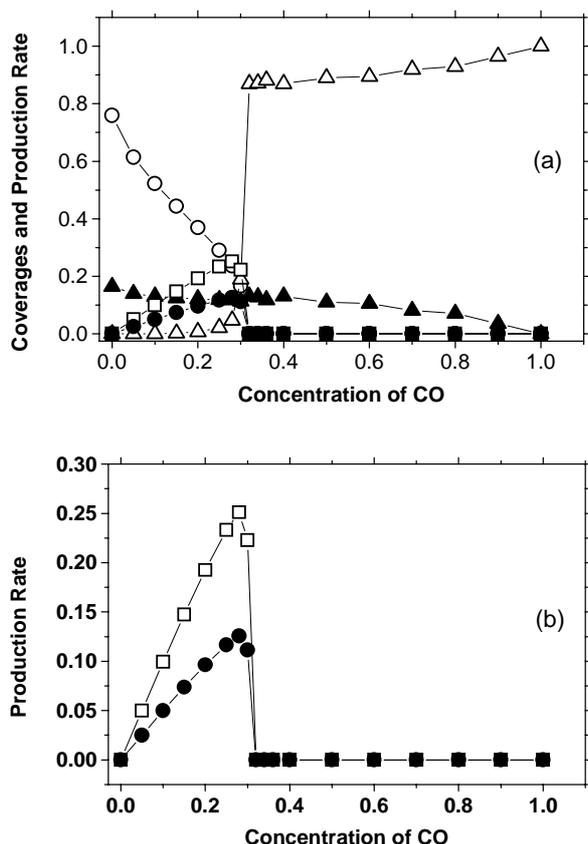


Figure 2. (a) Coverages of surface O (open circles), CO (open triangles), and N (closed triangles) for the model A. (b) Production of  $CO_2$  (open squares) and  $N_2$  (closed circles) versus CO partial pressure for the model A.

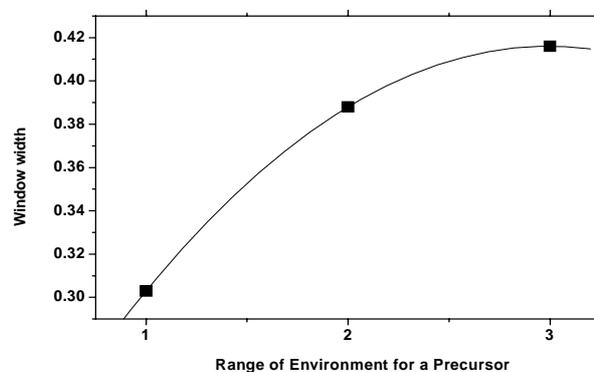


Figure 3. Window width vs range of precursor mobility

For higher concentration of CO and in higher environment, fewer CO precursors end their life as  $CO^S$  as compared with the first environment and hence NO molecule can find more vacant pair for their adsorption. This is the prime reason which plays a role in shifting  $y_2$  towards higher value of  $y_{CO}$ . Consequently a steady reactive window gets larger than that of LH mechanism and this fact is shown in Fig. 5.

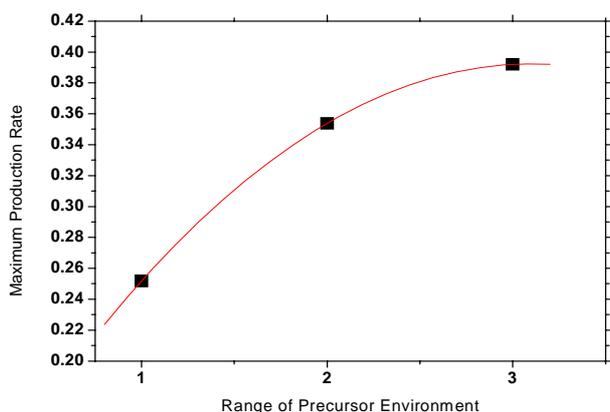


Figure 4. Maximum production rate vs range of precursor mobility

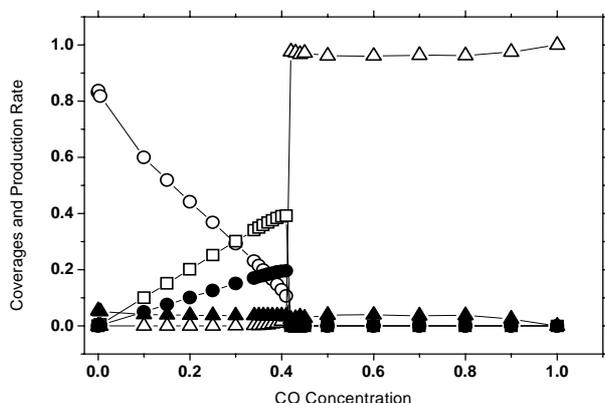


Figure 5a. Same as in figure 1(a) for Precursor mobility in third environment (model C)

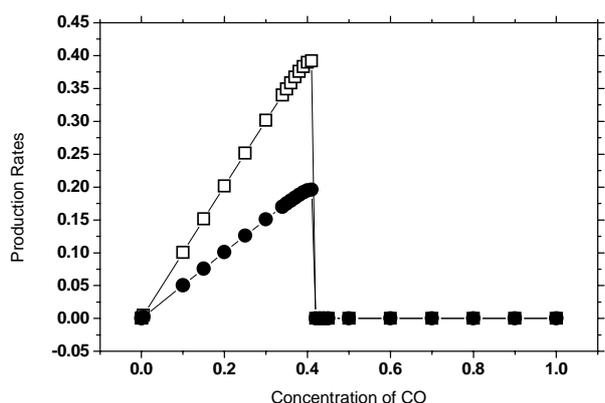


Figure 5b Same as in figure1 (b) for third environment (model C)

Next we consider the combined effect of the precursor of CO and diffusion of N on hexagonal surface. This combined effect is shown in Fig. 6.

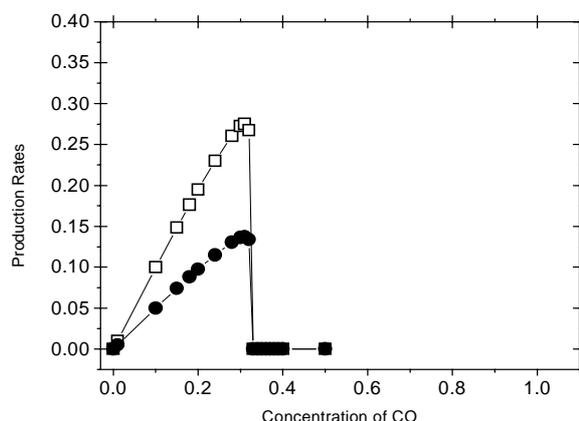


Figure 6. Production of CO<sub>2</sub> (open squares) and N<sub>2</sub> (closed circles) versus CO partial pressure for the Precursor of CO in the first environment and with diffusion of N.

The effect of diffusion of CO was also studied and it was observed that diffusion of CO has no effect on hexagonal lattice, and it confirms the observation made by Khan et al. [21] that the diffusion of CO has no effect on square lattice. However, it is observed in Fig. 6 that diffusion of N slightly shifts  $y_2$  towards higher concentration of CO.

### 5. Conclusions

It is concluded that with the introduction of non-thermal mobility (precursor mechanism), some additional features such as enhancement of SRS and increase in production rates are observed for CO-NO catalytic reaction that were not seen by considering the thermal (LH mechanism) model. It has been also observed that reactive window even increases by increasing the range of precursor mobility. Moreover, for a specific range of precursor mobility (1st, 2<sup>nd</sup> or 3<sup>rd</sup>), diffusion of N slightly shifts  $y_2$  towards higher concentration of CO.

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