

THE EFFECT OF ELEY RIDEAL MECHANISM ON CO-NO CATALYTIC SURFACE REACTION FOR A HEXAGONAL LATTICE: A MONTE CARLO SIMULATION STUDY

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A Monte Carlo simulation for CO-NO heterogeneous catalytic reaction over a square lattice as well as hexagonal lattice has already been performed with a model based on the Langmuir- Hinshelwood mechanism. Similarly this reaction on square lattice has also been studied by Eley-Rideal mechanism. Here Monte Carlo simulation has been used to study the effect of Eley-Rideal mechanism on a hexagonal lattice for CO-NO reaction. The reactive window gets enhanced due to this mechanism. It is observed that whenever ER mechanism is introduced, the production of CO₂ and N₂ starts as soon as the CO partial pressure (y_{CO}) departs from zero, which verifies the experimental observation. Moreover, the maximum production rate increases with the increase of ER probability.

Keywords: Monte Carlo simulation, Eley-Rideal mechanism, CO₂, Carbon monoxide

1. Introduction

Computer Simulation is one of the techniques employed to study heterogeneous catalysis. Ziff, Gulari and Barshad [1] introduced a Monte Carlo simulation technique now popularly known as the ZGB model to study the oxidation of carbon monoxide on catalytic surface. In this model the reaction occurs via Langmuir-Hinshelwood (LH) mechanism, 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 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. The range ($y_2 - y_1$) is window width. The transition at y_1 is of second order while the transition at y_2 is of first order. A controversial feature of the ZGB model concerns the second-order phase transition (SOPT), which has never been observed experimentally in the CO oxidation. Experiments

show that production of CO₂ starts as soon as CO concentration departs from zero [2, 3].

Following the ZGB model, several attempts have been made in order to give more realistic description of the model and its variants [4-14]. Together with the oxidation of CO, there has also been interest in the oxidation of CO by NO. Based on the ZGB model, another monomer-dimer (MD) reaction in which NO reacts with CO was simulated on different surfaces. For this type of reaction, the simple square lattice does not support the steady reactive state provided N atoms undergo diffusion [29] while two transition points are observed for hexagonal lattice. Yaldrum and Khan [15,16] have found that the second order phase transition (SOPT) takes place at $y_1 = 0.185 (\pm 0.002)$ and first order phase transition (FOPT) takes place at $y_2 = 0.338 (\pm 0.002)$.

It has been emphasized by many authors that non-thermal processes are also important to understand the catalytic reactions [17-21]. These processes include the Eley-Rideal (ER) mechanism (a direct reaction between a gas phase atom and an adsorbed atom) and the precursor

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mechanism of the surface reactions, which 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 [22] has also explored the effect of ER process on the simple ZGB model for the catalytic oxidation of CO by oxygen.

Khan and Ahmad [23] have also employed Monte Carlo simulations to explore the effects of Eley-Rideal (ER) mechanism on a simple Langmuir-Hinshelwood model for CO-NO catalytic reaction on a square surface. Without diffusion of CO and N and desorption of CO, they have shown that the model generates a very small reactive window of the order of 0.033. In ER mechanism, a gas phase reactant, never in equilibrium with the surface, directly picks up an atom of the adsorbed reactant and forms a product that leaves the surface. L. Olsson, et al. [24] have also carried out study to see the role of steps in CO-NO reaction on (111) surface of noble metals. By means of Monte Carlo simulation, Khalid et al. [25] have shown that the steady reactive state is observed in the usual LH mechanism for CO-NO catalytic reaction on Body Centered Cubic Lattice.

The objective of this manuscript is to explore the effects of ER mechanism on the phase diagram of the LH mechanism for CO-NO catalytic reaction through Monte Carlo simulation on hexagonal surface. The paper is structured as follows: In the next section, the reaction model and the simulation procedure is discussed. The results are presented and discussed in Section 3. Finally, the conclusions are given in Section 4.

2. Model and Simulation

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



Whenever Eley-Rideal mechanism is taken into the consideration then following step is simulated



Here (g), and S indicate gas phase and active surface sites respectively; while X^{S} , represent X adatom on the surface. In our Model steps 1-.5 are considered. 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 overall qualitative features of the phase diagram; it slightly increases the critical values [26]. Periodic boundary conditions are applied in order to avoid the boundary effects. The simulation starts with clean surface and proceeds as follows: The relative impingement rates of CO or NO on the surface sites are selected randomly with probability y_{CO} or $1 - y_{\text{CO}}$ to be proportional to their partial pressures respectively in such a way that the total probability is normalized to one. Such normalization implies that the model has a single parameter that is usually taken to be y_{CO} . Here y_{CO} is the concentration of CO in an infinite reservoir. 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 of the NN sites are occupied by O^{S} then the reaction step (4) takes place 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. If the selected site is occupied by N^{S} , then the trial ends.
- b. If CO happens to be selected and the randomly selected site is already occupied by CO^{S} , then the 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) and the trial ends. In this case if the reaction takes place then the one site occupied by O^{S} will be vacated.
- c. 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 to 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 (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 $CO_2(g)$.

The equilibrium coverages are measured as a function y_{CO} . To locate the critical points, ten independent runs each upto 50000 Monte Carlo (MC) cycles are carried out. If all the ten runs complete 50000 cycles without the lattice becoming poisoned, 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 obtain the coverages in SRS, the initial 10000 MC are ignored and the system is allowed to run up to 50,000 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 Discussion

The numerical results of reaction steps 1-4 of LH type for CO-NO catalytic reaction on the hexagonal lattice have already been presented by Yaldram et al [15]. With this simple LH mechanism for CO-NO catalytic reaction over the hexagonal lattice, the second order phase transition takes place at $y_1 = 0.185 \pm 0.002$, while the first order phase transition takes place at $y_2 = 0.338 \pm 0.002$. In LH model for low CO (high NO) partial pressure, surface contains cluster of oxygen atoms with N atoms trapped in these clusters. The ER mechanism breaks these clusters and a different situation is observed in the simulation for CO-NO catalytic reaction on the hexagonal lattice when ER mechanism with reaction step (5) is introduced. In the ER mechanism, the CO molecule in gas phase starts consuming the chemisorbed oxygen atoms trapped in N^S-N^S pairs and consequently isolated vacancies are created. Then each 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 the CO molecules can occupy these sites very easily. Consequently indirect supply of CO gas increases. Therefore, once CO molecule is chemisorbed on the vacant site, it triggers the reaction step (4). In this way, by the addition of ER mechanism, the consumption of oxygen increases, which increases the CO adsorption rate. Meanwhile, the chance of adsorption of NO on vacant site decreases as it needs two vacant sites for its adsorption, and therefore y_1 shifts toward lower concentration of CO as compared to LH mechanism. By increasing the CO concentration further, CO begins sitting on the surface alongwith N atoms and we observe a situation as shown in Fig.1(a) that indicates the snap shot for $y_{CO} = 0.33$. In this situation the chemisorbed oxygen atoms have already been burnt completely and surface is poisoned with combination of CO^S and N^S .

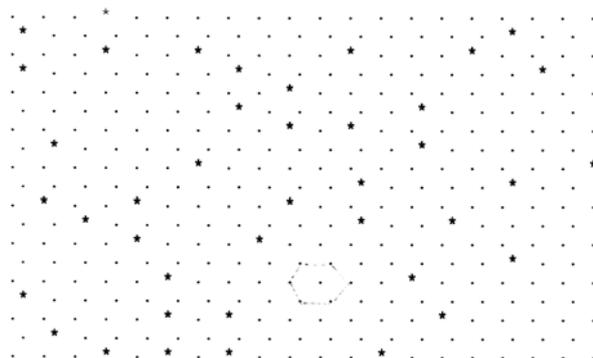


Figure 1. (a) A fraction of the snapshot for LH +ER (100%) for CO-NO on hexagonal lattice at $y_{CO} = 0.33$; where . for CO and * for N.

The lowest value of y_{CO} considered in our simulation was $y_{CO} = 0.005$. At this value, with the introduction of ER mechanism the equilibrium state of the system was in the steady reactive state. We therefore, assume that with the introduction of ER mechanism, the reactive state starts immediately for a non-zero value of y_{CO} . Thus the productive activity starts as soon as $y_{CO} \neq 0$, which confirms experimental observation [27]. Engel [28] performed the experiment on Pd surface by impinging molecular beam on the surfaces and compared the reaction step (4) with reaction step (5) and has shown that reaction step (5) is very fast in the region where the coverage of adsorbed oxygen is high. The LH mechanism (reaction steps 1-4) is effective when the coverage of CO and oxygen is very low. This is why the reaction step (5)

becomes very fast in the region with high coverage of adsorbed oxygen and it is consistent with the experimental observation.

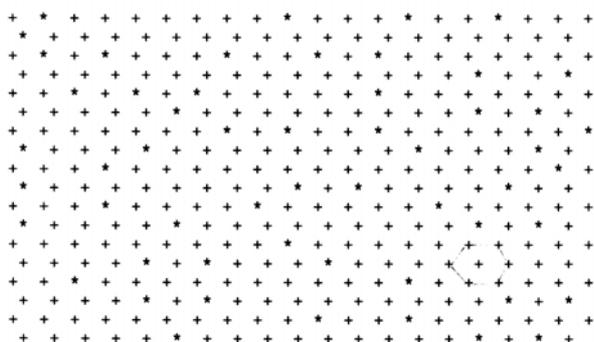


Figure 1b. A fraction of the snapshot for LH model for CO-NO on hexagonal lattice at $y_{CO} = 0.15$; where + for oxygen and * for N.

Fig. 1(b) shows the snapshot for $y_{CO} = 0.15$ in the simple LH mechanism for CO-NO catalytic reaction on the hexagonal lattice. This snapshot shows that at $y_{CO} = 0.15$, there is comparatively high coverage of O^S atoms on the surface. Therefore, in this region, the ER mechanism plays a dominant role in a region with high coverage of adsorbed oxygen.

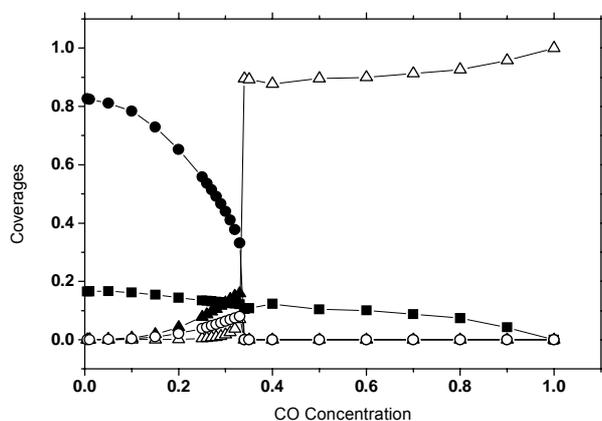


Figure 2a. Coverages of surface O (closed circles), CO (open triangles), N (closed squares) and Production rates of CO_2 (closed triangles), N_2 (open circles) with ER 1%.

Fig. 2 (a-b) shows the situation when the reaction step (5) with ER step probability P_{ER} of 0.01 is taken into consideration. In the case, when $P_{ER} = 0.01$, and $y_{CO} = 0.005$, the system enters an SRS with continuous production of CO_2 and N_2 . However, when $y_{CO} = 0.08$, an indicative production

rate starts. As y_{CO} (concentration of CO) increases further, the coverage of O^S and N^S decreases, while the production rate increases and it keeps on increasing until $y_{CO} = 0.33 \pm 0.005$, where it rapidly decreases to zero and the surface is covered by CO^S and partially by N^S . This means that a very small value of P_{ER} has a significant effect on the catalytic reaction system. Fig.3 (a-b) shows the situation at $P_{ER} = 0.10$, where a significant production of CO_2 and N_2 starts the moment y_{CO} departs from zero and it continues till $y_{CO} = 0.33 \pm 0.005$. With further increase in ER steps probability P_{ER} , y_2 shifts very slightly from 0.33 ± 0.005 to 0.30 ± 0.005 .

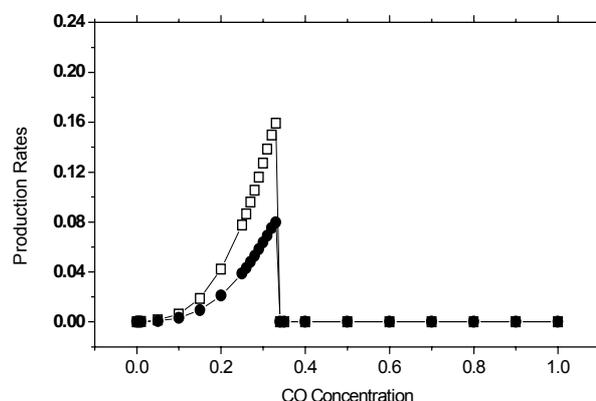


Figure 2b. Production Rate for ER 1%. CO_2 (open squares), N_2 (closed circles).

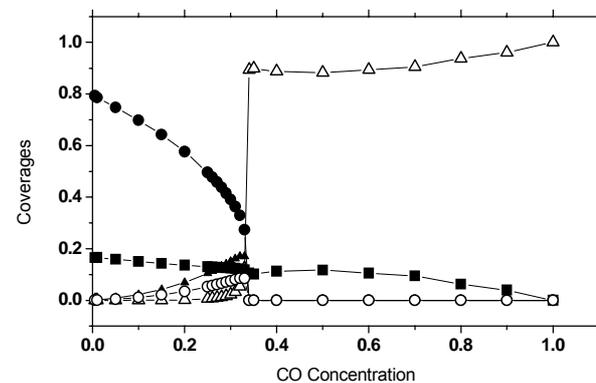


Figure 3a. The same as Fig. 2(a) but for ER 10%.

Fig. 4(a-b) shows the results corresponding to reaction step (5) with ER step probability 100%, where the coverages of the species and production rates are plotted as a function of y_{CO} . It shows the value of $y_1 \approx 0.00$ and $y_2 = 0.300 \pm 0.005$. This indicates that the steady reactive window of width 0.300 ± 0.005 is found when ER mechanism is introduced which is larger than that of the window

observed in LH mechanism [15, 16]. It appears from Figs.(2)-(4) that the coverages of surface oxygen decreases more rapidly as ER step probability increases. Moreover, production rate increases with the ER step probability (Fig. 5).

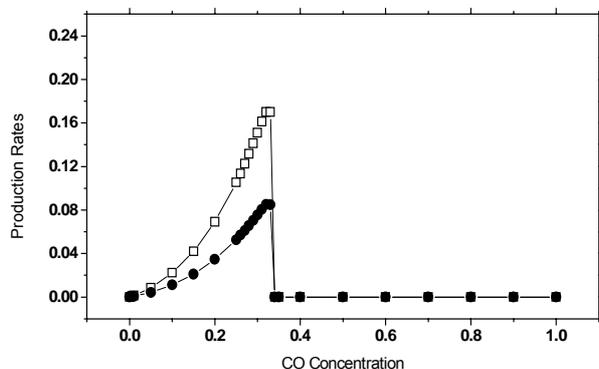


Figure 3b. The same as Fig.2(b) but for ER 10%.

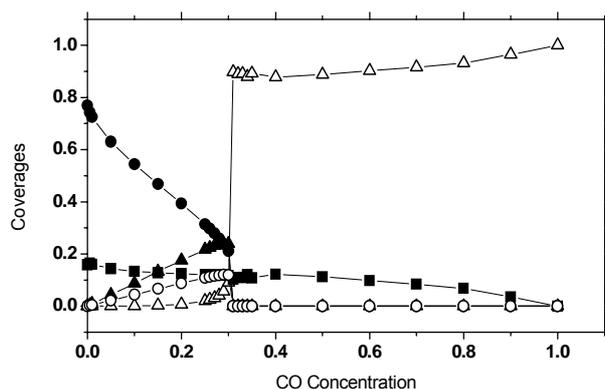


Figure 4a. The same as Fig. 2(a) but for ER 100%.

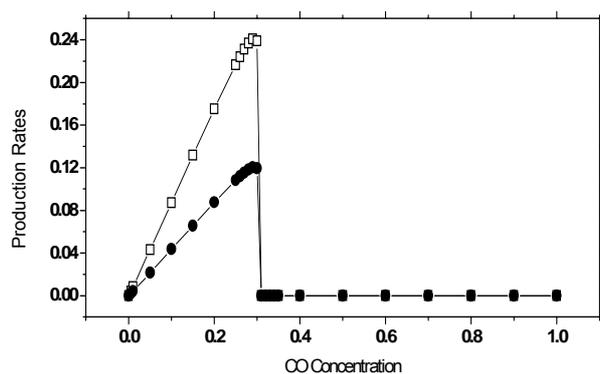


Figure 4b. The same as Fig. 2(b) but for ER 100%.

4. Conclusions

A detailed analysis of ER mechanism for the CO + NO on the hexagonal lattice has been carried

out, in which a reactant (CO) in gas phase directly picks up an O^S (atom) from the surface and forms

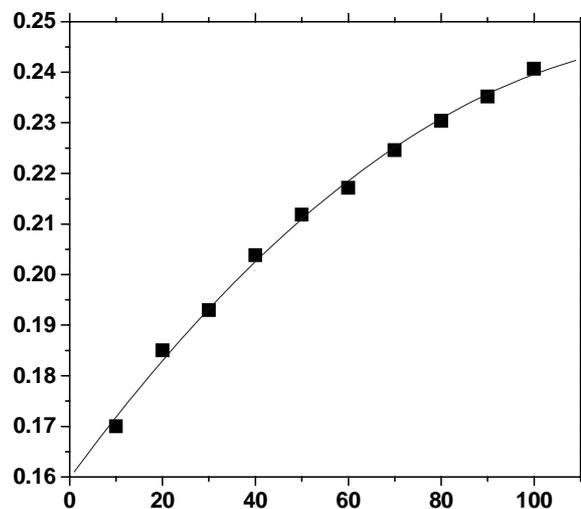


Figure 5. Maximum Production rate of CO_2 versus ER-step probability.

the product CO_2 that leaves the surface immediately. This mechanism incorporates some interesting results on the phase diagram of CO-NO catalytic reaction on the hexagonal lattice, which were not seen by considering the LH model only. The usual SOPT disappears and continuous production of CO_2 and N_2 gas starts the moment CO concentration departs from zero. The results are compared with LH mechanism and it is concluded that with the introduction of non-thermal process (ER mechanism), some additional features such as enhancement of SRS and increase in production rate are observed for CO-NO catalytic reaction. The results obtained by ER mechanism are close to the experimental observation.

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