



ELEY-RIDEAL MODEL FOR MONOMER-DIMER SURFACE CATALYTIC REACTION: STUDY OF SUBSURFACE EFFECTS

* A.U. QAISRANI and M. KHALID

Department of Physics, Gomal University, D.I. Khan, Pakistan

(Received January 30, 2003 and accepted in revised form April 23, 2003)

We have investigated the effects of the Eley-Rideal (ER) process on the phase diagram of the Langmuir-Hinshelwood (LH) type monomer-dimer (CO-O₂) surface-subsurface model. With the consideration of a new pathway in which oxygen molecule (dimer) is adsorbed in such a way that it takes one surface site whereas second site may be from surface or from subsurface. In this case the qualitative trend of surface oxygen coverage is consistent with the experimental situation i.e. the coverage of surface oxygen decreases slowly with increase in concentration of CO (y_{CO}). Moreover, the production of CO₂ can be predicted in the form of a mathematical relation.

Keywords: Catalysis, Monte Carlo simulation, Carbon monoxide, Oxygen, Eley-Rideal, ZGB model.

1. Introduction

In the recent years a number of computer models have been proposed to study catalytic surface reactions. A simple monomer-dimer (MD) model has been proposed by Ziff, Gulari and Barshad [1], which is known as ZGB model. This model has been used to study CO-O₂ reaction system. A reservoir containing CO and O₂ in a given proportion is in contact with the surface, which is modeled with a square lattice. It is assumed that the supply of the gas is inexhaustible. A monomer (CO) on striking the surface adsorbs onto a single vacant site, while a dimer (O₂) adsorbs onto two adjacent vacant sites. Whenever an oxygen atom finds itself sitting next to a CO atom, a reaction between CO and O₂ takes place with the formation of CO₂ that desorbs from the surface leaving behind two vacant sites. The reaction mechanism exhibits two phase transitions y_1 and y_2 . At the feed concentration of CO (y_{CO}) less than y_1 , the surface is completely covered with oxygen and if the feed concentration of CO is greater than y_2 , the lattice is filled with CO. Only in the range $y_1 < y_{CO} < y_2$ does the system exhibits a steady reactive state (SRS). The transition at y_1 is continuous while at y_2 it is discontinuous. This model involves only one parameter i.e. the feed concentration of CO. This simple model shows some physical properties, which are observed in real systems such as the

poisoning with CO of the catalyst.

Ever since the introduction of the Ziff, Gulari and Barshad (ZGB) gas-lattice model [1] for the heterogeneously catalyzed CO-O₂ reaction, the study of reactive processes using Monte Carlo simulation has undergone a rapid growth [2-7]. 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 the reaction rate begins to increase as soon as the concentration of CO departs from zero [7-9]. Bagnoli et al. [8] have shown that one can annihilate this SOPT within the ZGB model by involving very specific local interactions. Lately, the presence of subsurface oxygen on Pt (100) and Rh (110) has been observed experimentally in the reaction [10-12]. Some authors have also used the presence of subsurface oxygen to explain the kinetic oscillations in the catalytic CO oxidation on Pd (110) surface [13, 14]. Recently, Khan et al. [15] have carried out a Monte Carlo simulation study to see the effect of a subsurface, on the CO-O₂ surface catalytic reaction by introducing various reaction mechanisms. Some of these reactions are not interesting in the sense that they reproduced the same general features as those of the ZGB model except for a shift in the transition points without any significant change in the width of the reactive window. However, the hypothetical

* Corresponding author : nadikyears@yahoo.com

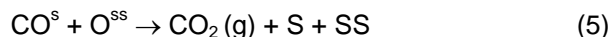
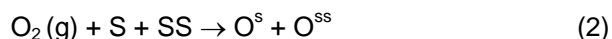
conjecture, in which an oxygen dimer adsorbs on one surface site and a subsurface site while a CO molecule sitting on the surface reacts with the subsurface oxygen, in addition to the normal surface reactions, seems to generate features in the model that bring it closer to real systems.

The transient non-thermal mobility caused by the inability to instantaneously dissipate the energy gained by a particle after formation of the surface bond seems to be a common process in nature. A class of such catalyzed reactions is imagined to proceed via the Eley-Rideal (ER) [16] mechanism, in which 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. This class of reaction, halfway between the gas phase type and Langmuir-Hinshelwood (LH) [17] type is of immense interest in surface science. Jackson and Persson [17] have studied the dynamics of a 'hot' hydrogen dimer in ER process (the direct reaction between a gas phase H atom and an adsorbed H atom) using a fully three-dimensional flat surface model for Cu (111). Meakin [18] explored the effects of the ER process on the simple ZGB model for the catalytic oxidation of CO by oxygen. The ER process results in the formation of a new regime in which a continuous reaction can be sustained. The moment CO partial pressure departs from zero a continuous production of CO₂ starts. This production continues till $y_{CO} \approx 0.497$, where a first order phase transition terminates this activity and the surface is poisoned (fully occupied) by CO. By means of ER process, he also studied monomer-monomer reaction system and got similar results [18].

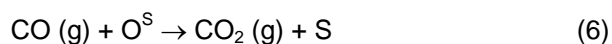
The objective of this manuscript is to explore the effects of the ER process on the phase diagram of the LH type surface-subsurface model for CO-O₂ catalytic reaction system. The paper is structured as follows: In the next section the reaction model and the simulation procedure is discussed. The results are presented and discussed in section 3. Finally the conclusions are inferred in section 4.

2. Model and Simulation

The usual simple LH surface-subsurface model of the system can be written in the form of the following equations [15]:



With the introduction of Eley-Rideal process, one has to add the following equation:



Here (g), S and SS indicate gas phase, active surface and subsurface sites respectively while X^{S} and X^{SS} represent X adatom on the surface and subsurface respectively. There appears to be considerable uncertainty concerning the relative importance of LH and ER reaction steps given by equations (4) and (6) respectively [19, 20]. It is worthwhile to mention that the relative frequency of LH reaction step and the ER reaction step depends upon oxygen coverage. If the initial oxygen coverage on the surface is higher (small y_{CO} values), then ER reaction step becomes dominant otherwise LH reaction step becomes important [21]. We have investigated the addition of reaction step (6) to the usual simple LH surface-subsurface model of the reaction system.

The relative partial pressures or concentrations of CO and O₂ are y_{CO} and y_{O_2} respectively ($y_{CO} + y_{O_2} = 1$). We consider a simple cubic structure. We use two layers of square lattices so that each surface site (upper layer site) has a subsurface site (lower layer site) just below it. We take the lattice size $L=128$ for each layer. It is observed that an increase in the lattice size changes the critical values slightly but overall qualitative nature of the phase diagram is not affected [20]. The precise value of the critical point is, however, more important in the study of dynamic and static critical exponents. For each surface, periodic boundary conditions are employed to avoid the boundary effects. According to this model scheme, each surface site S has five first nearest neighbours (nn); four on the surface and one in the subsurface just below S. In the present work, the simulation starts with a clean surface and a clean subsurface. 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 were carried out. If all the ten runs proceed up to 50,000 MC cycles without the lattice being poisoned (fully occupied), the

particular point is considered to be within steady reactive state (SRS). The poisoning of even a single run is a sufficient criterion for considering the point to belong to the poisoned state. If the run does not end up in a poisoned state, then in order to get the coverages corresponding to the SRS, the initial 10,000 MC cycles 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 rate) is an average taken over 4000 configurations.

The steps involved in the simulation are a surface site S is selected at random. (a) If CO happens to be selected, then one of these events may occur: (i) if the randomly selected site is vacant then CO is adsorbed on it (CO^{S}) via step (1). Five nn sites (four on the surface and one in the subsurface) of the adsorbed CO molecule are scanned randomly for the presence of O^{S} or O^{SS} . If any of the nn sites are occupied by O^{S} then the reaction step (4) takes place otherwise the presence of O^{SS} leads to the reaction step (5) and the trial ends. In the first case two surface sites are vacated whereas in the second case one site each from surface and subsurface are vacated. (ii) If the randomly selected site S is occupied by an O^{S} atom then the CO (g) molecule in gas phase directly reacts with it with some probability P_{E} in order to complete the ER step (6) and the trial ends. In this case if the reaction takes place then the site occupied by O^{S} will be vacated. (b) If O_2 happens to be selected and if the randomly selected site S is occupied, then the trial ends. In case the randomly selected site S is vacant then another vacant site is required to adsorb the O_2 molecule in atomic form. For this purpose we have considered two cases. (a) A second vacant site is picked randomly from five nn sites of S . (i) If the second vacant site is on the surface then O_2 adsorbs in atomic form on these two surface sites (reaction step 3). (ii) The surface nn sites of these two atoms (O^{S}) are scanned for the presence of CO^{S} to complete reaction step (4). (iii) If the second vacant site is in the subsurface then one O atom is adsorbed on the surface (O^{S}) and the other atom is adsorbed in the subsurface (O^{SS}). Surface nn sites of O^{S} are scanned for the presence of CO^{S} to complete the reaction step (4) (here it may be noted that CO^{S} can only be found on the surface). However, the surface nn of O^{SS} cannot contain CO^{S} . Therefore it is not scanned for the possibility of reaction step (5). This O^{SS} atom remains in the subsurface reservoir. (b) The second vacant site is

always taken from subsurface. If the subsurface nn site of the site S is occupied then the trial ends and a new molecule is selected. If a subsurface nn site is vacant, then the O_2 molecule dissociates into O^{S} and O^{SS} . The four-nn sites of O^{S} are then scanned randomly (as discussed above) for the presence of CO^{S} in order to complete reaction steps (4).

3. Results and Discussion

Khan et al. [15] have already presented the numerical results of the surface and subsurface of a simple cubic structure of simple LH model. An interesting situation is observed when steps (1), (2), (4) and (5) of surface-subsurface model are considered. For $y_{\text{CO}} = 0$, the surface as well as subsurface are totally covered by oxygen but the moment $y_{\text{CO}} \neq 0$, a continuous formation of CO_2 takes place and it keeps on increasing till $y_{\text{CO}} = 0.4$. Then, it starts decreasing quite rapidly until $y_{\text{CO}} = 0.50$ where it stops and the surface is completely covered by CO while the subsurface becomes totally empty. This trend of CO_2 production is consistent with the experimental situation. However, in this case when $y_{\text{CO}} \neq 0$, the coverage of surface oxygen drops sharply from 1.0 to 0.4, which is not seen in the experimental situation. It is observed in experiments that the coverage of surface oxygen decreases slowly with increase in y_{CO} . Khan et al [15] have also shown that when steps (1), (2), (3), (4) and (5) are considered, the qualitative situation becomes similar to that of ZGB model. Only the transition points (y_1 and y_2) are shifted towards higher values of y_{CO} whereas the window width remains same as that of ZGB model. The values of transition points are $0.420 (\pm 0.001)$ and $0.552 (\pm 0.001)$ respectively. In the present model, we will lay emphasis on the effect of ER step on the phase diagrams of the above-mentioned two situations of Khan et al. work. The effect of CO diffusion and desorption will also be discussed.

Model A Steps (1), (2), (4), (5) and (6)

Figure 1 shows the situation when the probability of ER step is taken to be 0.01 (top) and 1.0 (bottom) respectively. The situation is same qualitatively as seen in the surface-subsurface model of Khan et al. [15]. However, in this case when $y_{\text{CO}} \neq 0$, the coverage of surface oxygen sharply drops from 1.0 to less than 0.2, which shows a rather worse situation as seen in Khan et al. [15] model. It can be seen that the qualitative nature of figure 1 is the same (i.e. the position of the critical transition points (y_1 and y_2) and

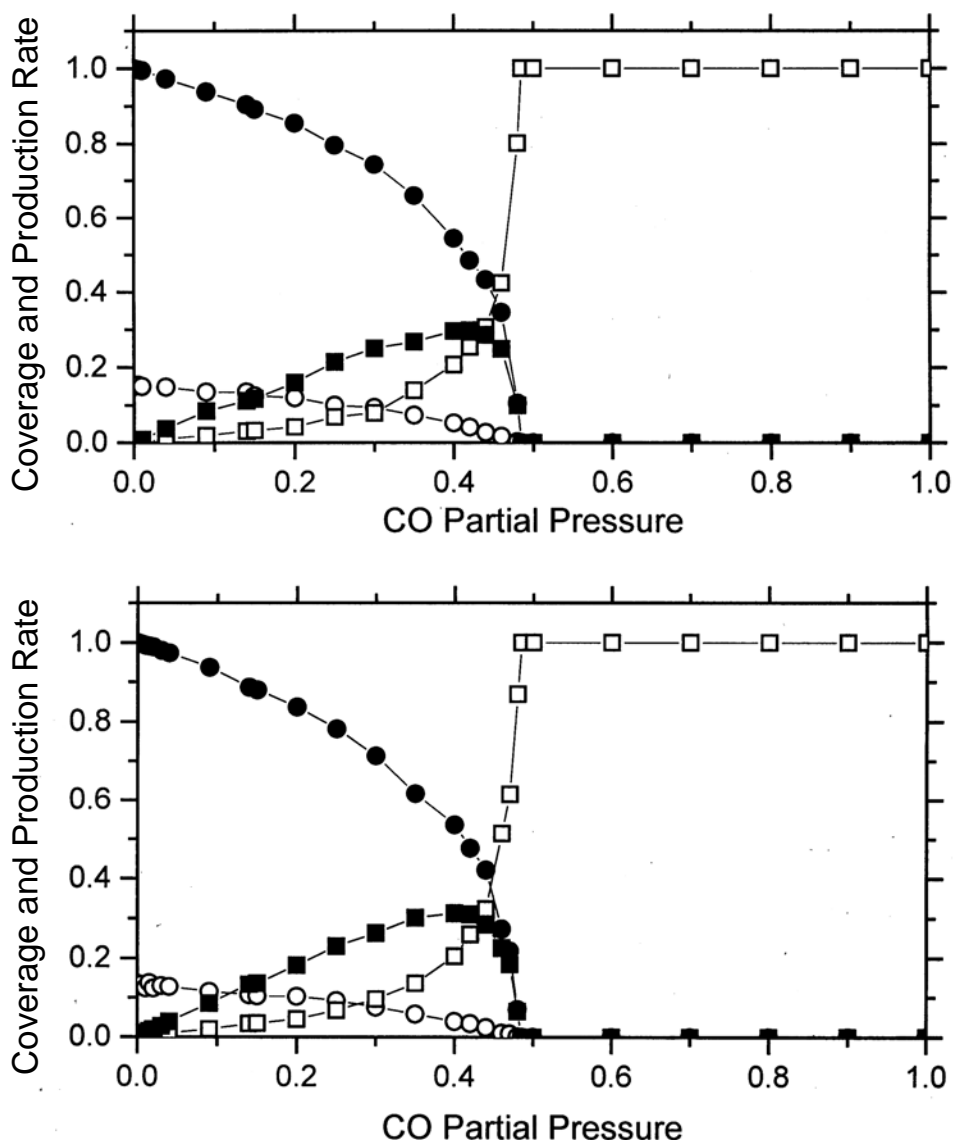


Figure 1 A plot of surface oxygen coverage (open circle), subsurface oxygen coverage (solid circle), CO coverage (open square) and CO₂ production rate (solid square) versus CO partial pressure for model A when the probability of ER step is taken to be 0.01 (top) and 1.0 (bottom) respectively.

quantitative values of coverages and production rate are the same) as compared to the surface-subsurface model of Khan et al. [15]. This means that the probability of ER step has no significant effect on the LH phase diagram of the system. This is because O₂ molecule has already been adsorbed as a pseudo monomer and the moment $y_{CO} \neq 0$ the surface oxygen burns readily as a result of the reaction step (4). However, with increase in ER step probability, the maximum production rate (R_{max}) slightly increases (Figure 2). It shows a behavior of the type $R_{max} = 0.308 + 0.034 P_E - 0.013$

(P_E)² (polynomial of degree 2) with standard deviation equal to 0.0008.

Model B Steps (1), (2), (3), (4), (5) and (6)

A fairly remarkable situation is observed in this case. Figure 3 shows the situation when the probability of ER step is taken to be 0.01 (top) and 1.0 (bottom) respectively. In the first case (when ER step probability = 0.01), for $y_1 < y_{CO} < 0.1$, the surface as well as subsurface are almost covered by oxygen but the moment $y_{CO} > 0.1$, a continuous formation of CO₂ takes place and it keeps on

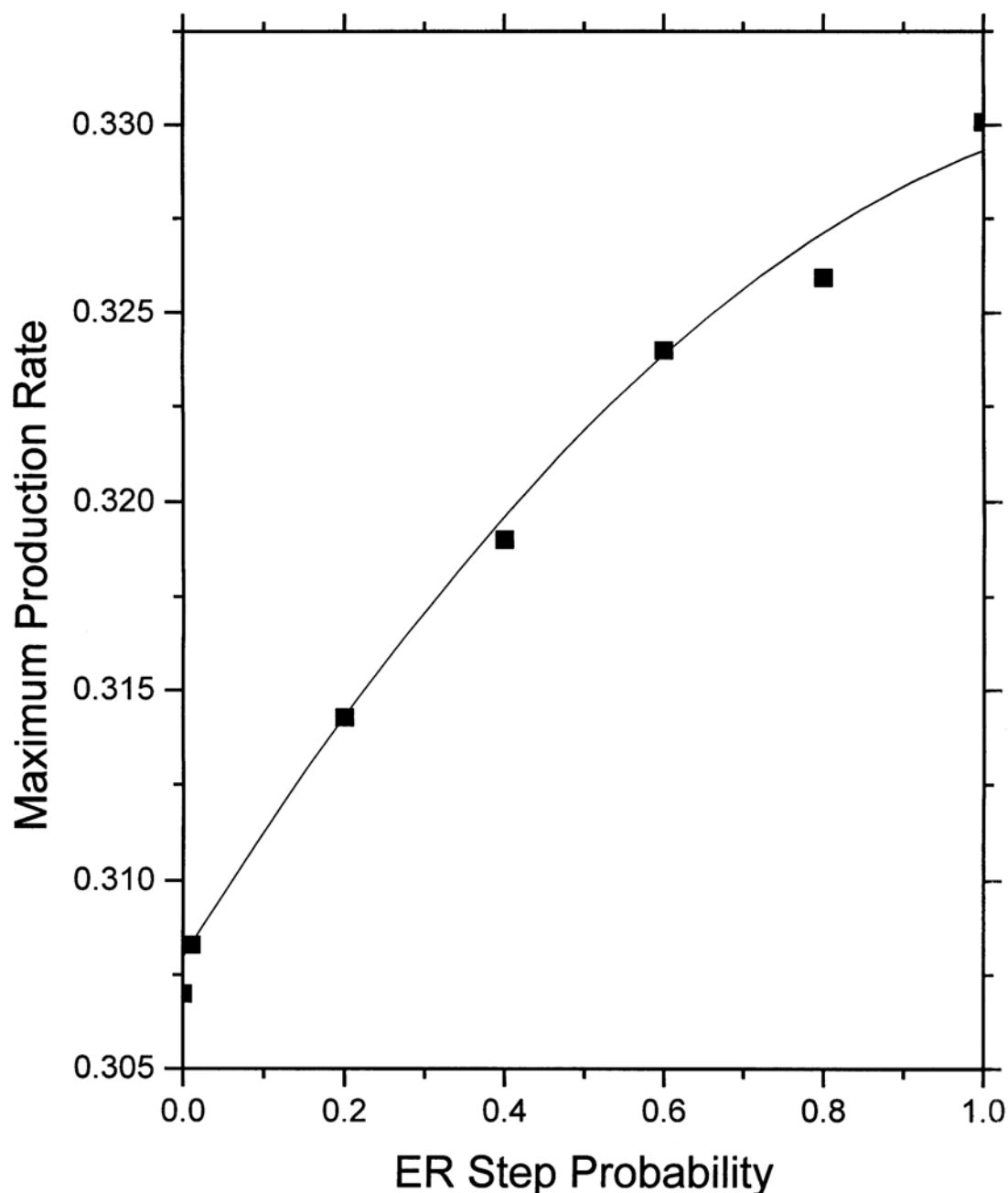


Figure 2. A plot of maximum production rate of CO_2 versus ER step probability for model A. A line of fit of the data is also shown.

increasing till $y_{\text{CO}} = 0.66$, where it rapidly decreases to zero and the surface is completely covered by CO while the subsurface is totally empty. This means that even a very small probability of the ER step has a significant effect on the LH phase diagram of the system. It increases the reactive region from 0.13 (as observed by Khan et al. [15] without ER step) to 0.55. With further increase in the probability of ER step, the value of y_2 remains

unchanged whereas the value of y_1 shifts towards a lower value of y_{CO} . Ultimately at ER step probability (PE) = 0.20, we get a situation where the production of CO_2 starts the moment y_{CO} departs from zero and it continues till $y_{\text{CO}} = 0.66$. This is consistent with the findings of Gates [19] that the ER reaction step becomes dominant when the initial oxygen coverage on the surface is higher (smaller y_{CO} values) otherwise the LH reaction

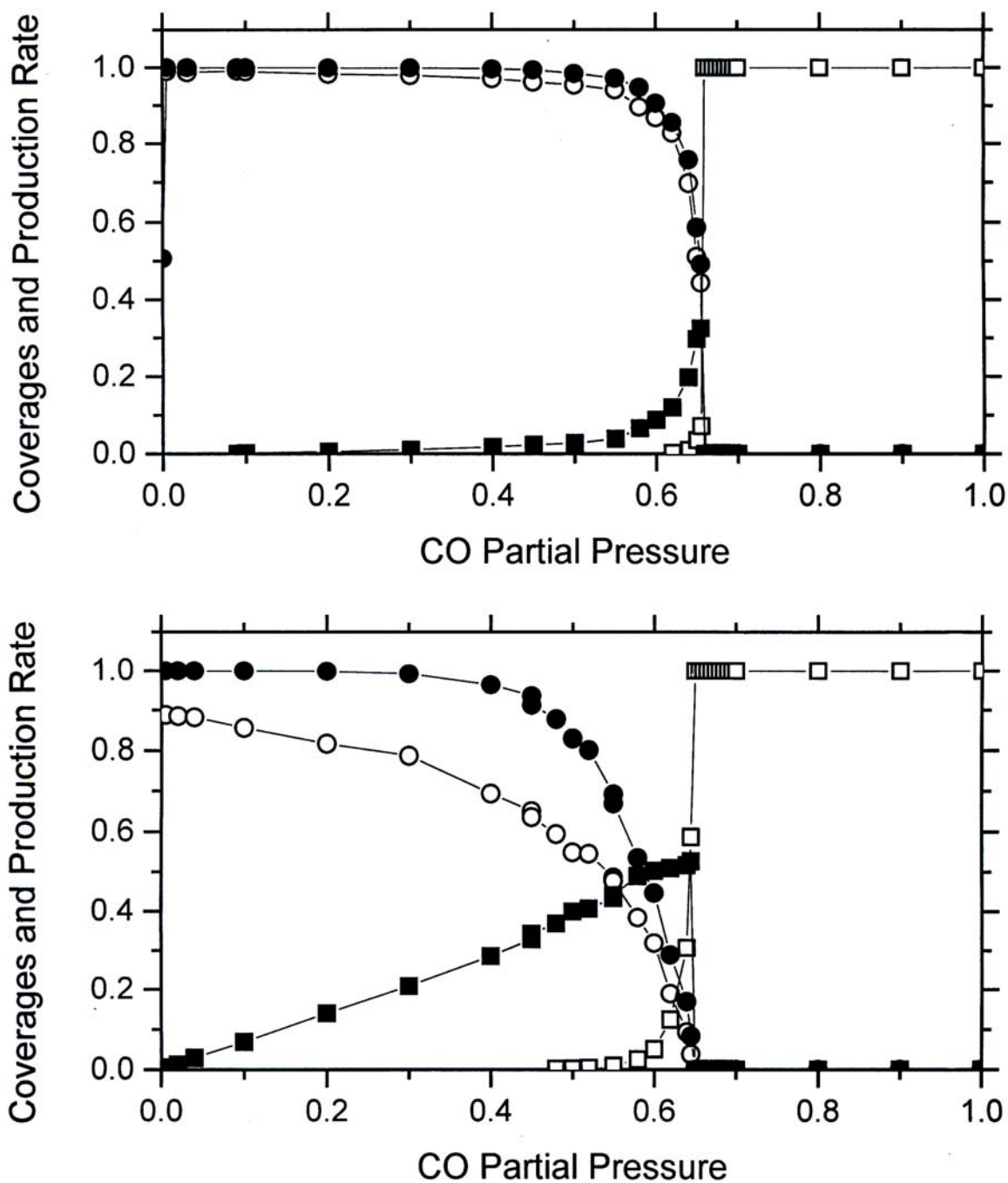


Figure 3. Same as in figure 1 for model B.

step becomes important. On the other hand an increase in the probability of ER step also increases the value of maximum production rate. It shows a behavior of the type $R_{\max} = 0.30 + 0.49 P_E - 0.26 (P_E)^2$ (polynomial of degree 2) with standard deviation equal to 0.012 (figure 4). The key feature of this figure is that the trend of surface oxygen coverage is consistent with the experimental

situation i.e. the coverage of surface oxygen decreases slowly with increase in y_{CO} . The other important factor of our study is that the production of CO_2 (R) can be written in the form of a mathematical relation. A behaviour of the type $R = 0.0036 + 0.582(y_{CO}) + 0.375 (y_{CO})^2$ (polynomial of degree 2) with standard deviation equal to 0.0098

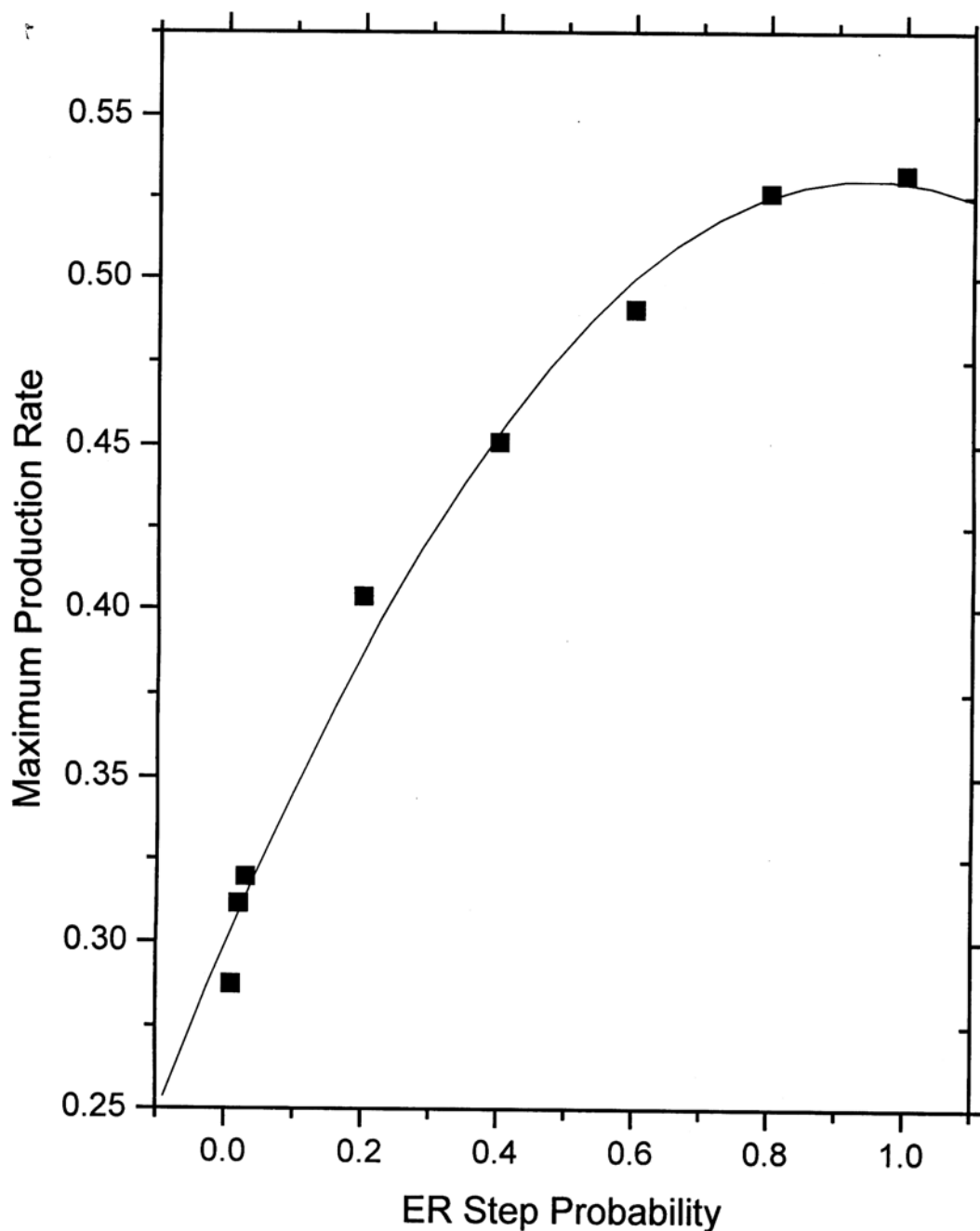


Figure 4. Same as in figure 2 for model B.

is observed when the data from the bottom of figure 4 ($P_E=1$) is fitted (figure 5).

4. Conclusions

We have investigated the effects of the ER process on the phase diagram of the LH type surface-subsurface model for CO-O₂ catalytic reaction system. We have considered two different models. In model A, oxygen molecule (dimer)

always adsorbs in atomic form by taking one surface and one subsurface site. In model B, oxygen molecule (dimer) is adsorbed in such a way that it takes one surface site whereas second site may be from surface or from subsurface. Model A does not improve the LH situation of the phase diagram of the system. However, in this model CO₂ production increases with ER step probability P_E . On the other hand model B shows

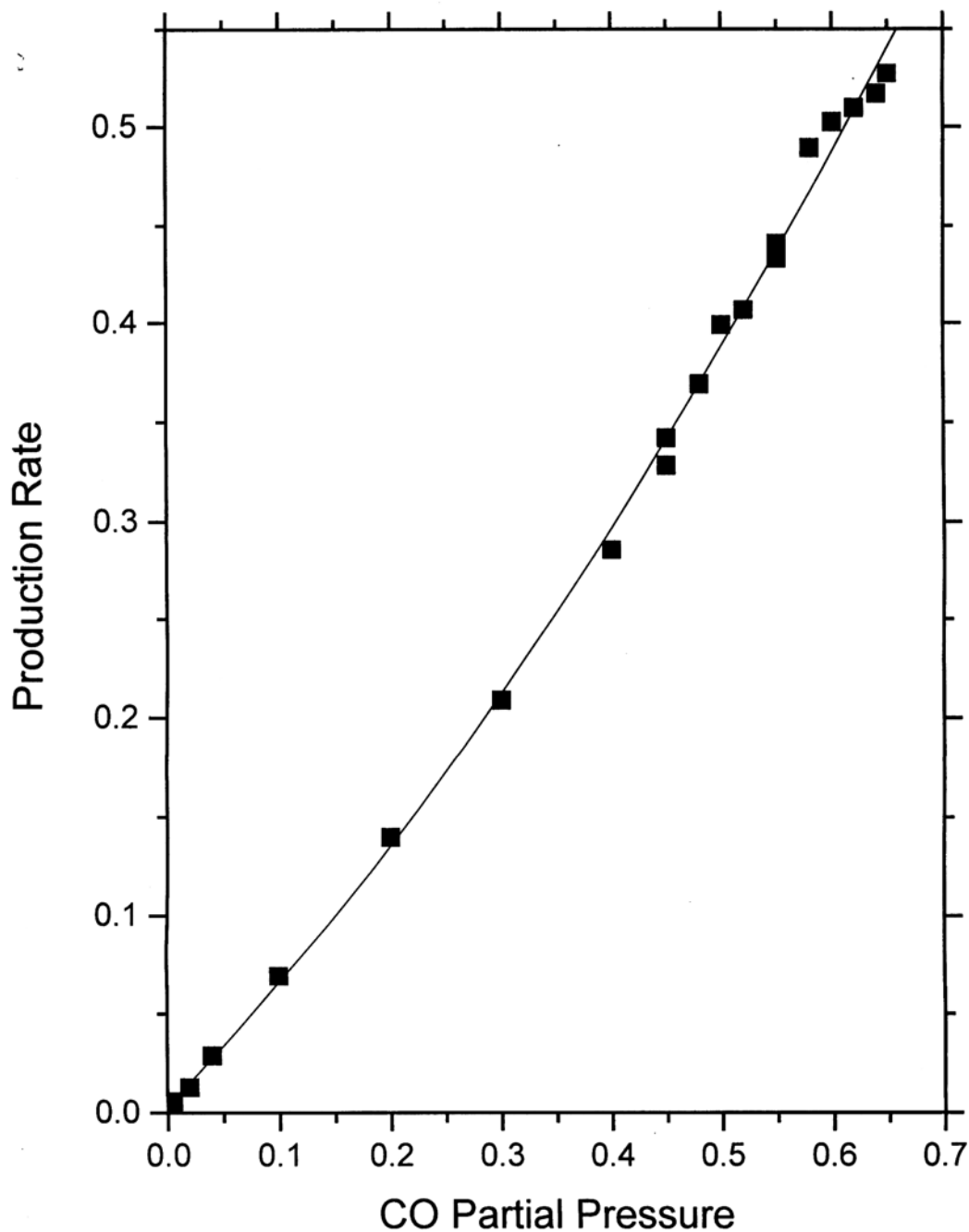


Figure 5. A plot of CO₂ production versus CO partial pressure for the case of model B when ER step probability is taken to be one. A line of fit of the data is also shown.

significant effect on the LH situation of the phase diagram of the system. The qualitative trend of surface oxygen coverage is consistent with the experimental situation i.e. the coverage of surface oxygen decreases slowly with increase in y_{CO} . The production of CO₂ can be predicted in the form of a

mathematical relation. Further detailed study is underway.

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