

## A PHASE DIAGRAM STUDY OF A SUPERFICIAL TRIMER-TRIMER CATALYTIC SURFACE REACTION

K. IQBAL, \*K.M. KHAN, M. PARVEZ<sup>1</sup> and P. AHMAD

Nuclear Physics Division, PINSTECH, P.O. Nilore, Islamabad, Pakistan

<sup>1</sup>Computer Division, PINSTECH, P.O. Nilore, Islamabad, Pakistan

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The phase diagram of a trimer-trimer model has been studied for a hexagonal lattice. We have also studied the effect of diffusion and desorption of the trimer on the phase diagram through Monte-Carlo simulation. The effect of desorption of the trimer shows similar behaviour as observed in the dimer-trimer model when desorption of the dimer is taken into account.

**Keywords :** Catalysis, Monte Carlo, Computer simulation, Trimer, Adsorption kinetics, Langmuir-Hinshelwood

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### 1. Introduction

An investigation of the lattice models of catalytic surface reactions is extremely helpful in gaining a better understanding into the kinetics of catalytic processes. Ziff, Gulari and Barshad [1], and Dumont et al. [2] have introduced a monomer-dimer (MD) model, which has been used to study a reaction system of the type  $2A+B_2 \rightarrow 2AB$ . This reaction mimics the catalytic oxidation of CO. This model is generally known as ZGB model. The only parameter in this model is the feed concentration  $y_A$  of the monomer (A). As a function of  $y_A$ , the system exhibits phase transitions at  $y_1$  (continuous) and  $y_2$  (discontinuous). A second-order phase transition (SOPT) at  $y_1 = 0.389 \pm 0.001$  separates a B-poisoned state from steady reactive state (SRS) while a first order transition (FOPT) at  $y_2 = 0.525 \pm 0.001$  separates an A-poisoned state from SRS. Within the window defined by  $y_1 < y_A < y_2$  the system exhibits SRS with continuous production of AB. The steady reactive state is defined as a domain in the parameter space where a steady production of AB is observed. Fixing all the parameters except  $y_A$ , the partial pressure of A, the width of the reactive window is defined as  $w = y_2 - y_1$  where  $y_1$  is the minimum value of  $y_A$  necessary for the reaction to be initiated, and where  $y_2$  is the value of  $y_A$  for which the reaction stops due a poisoning of the surface. Meakin and Scalapino [3] investigated the effect of lattice type on the reactive window of ZGB model. They found

that for a hexagonal lattice (each surface site has six nearest neighbours) the reactive window increases as compared to the usual square lattice with  $y_1 = 0.360 \pm 0.005$  and  $y_2 = 0.561 \pm 0.001$ .

If the physically relevant possibility of desorption of the reactants from the lattice surface is considered in addition to desorption of the reaction product then the system exhibits SRS which may be determined by the competition between reactant desorption and desorption of the reaction product [4,5], and which can be understood at the mean field level [5]. The kinetics of irreversible dimer-dimer (DD) surface reaction of the type  $1/2A_2 + 1/2B_2 \rightarrow AB$  with desorption of the dimer  $B_2$  has been studied by Khan et al. [6] on a square lattice. For the desorption probability (P) of  $B_2$  equal to zero, a single discontinuous transition separating an A + vacancies- poisoned state from a B + vacancies-poisoned state is obtained at  $y_B = 0.50$  ( $y_B$  is the feed concentration of the dimer  $B_2$ ). With increase in P a SRS, which is separated from the poisoned state by two continuous transitions, is obtained for this system. The position of the transition points depends upon the value of P. For P equal to one, a single continuous transition at  $y_B = 0.538$  separates a poisoned state from SRS. The reactive window width is sensitive to the value of P. With decrease in P,  $y_1$  remains almost constant whereas  $y_2$  shifts noticeably towards  $y_1$ . At  $P \approx 0.20$ , the transition points merge,

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\* Corresponding author : khalidk@pinstech.org.pk

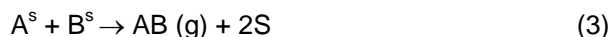
resulting in the disappearance of the reactive window.

Kohler and Avraham have reported results of a dimer-trimer (DT) model of the type  $2A_3+3B_2 \rightarrow 6AB$  on a hexagonal lattice [7]. They have observed a phase diagram in which a SRS is separated from an A + vacancies-poisoned state by a continuous transition ( $y_1$ ) and B + vacancies-poisoned state by a discontinuous transition ( $y_2$ ). The phase diagram seems to resemble qualitatively the standard ZGB model with the difference that for  $y_B < y_1$  ( $> y_2$ ) the surface is poisoned with 100 % A (B) in the ZGB model. However, a number of discrepancies can be found in their paper. In figures, the transition points  $y_1$  and  $y_2$  are shown at  $\sim 0.34$  and  $\sim 0.66$  respectively whereas in the discussion they quote these values as 0.3406 and 0.461 respectively. For the extreme case of  $y_A=1$ , their figure shows the coverage of dimer  $\sim 0.80$  whereas from the text it can be concluded that the coverage of dimer is  $\sim 0.914$ . From these discrepancies, Khan et al. [8] have concluded that Kohler and Avraham [7] have misquoted some of their results. Khan et al. [8] have studied the DT model on a square lattice to look into the effect of the lattice type on the phase diagram of the system. The steady reactive window width significantly decreases from 0.12 (for the hexagonal lattice as quoted by Kohler and Avraham) to 0.02 for the square lattice.

In this manuscript the effect of diffusion and desorption of a trimer on the phase diagram of another hypothetical (superficial) trimer-trimer (TT) reaction system has been reported. The purpose of this study is to get theoretical knowledge of the behaviour of the species on the surface in a trimer-trimer system and to explore the effects of desorption and diffusion on this reaction system so that more real but complicated systems like water gas shift reaction and the industrial preparation of methanol can be studied with better understanding. In addition, this study also gives us an insight into achieving the optimized production. The paper is structured as follows: In the next section, the reaction mechanism and the simulation procedure will be discussed. The results will be presented and discussed in section 3. Finally, the conclusions will be drawn in section 4.

## 2. Model and Simulation

Following three equations symbolically represent the TT model:



Here (g) and S indicate gas phase and active surface site respectively.

The relative partial pressures or concentrations of  $B_3$  and  $A_3$  are  $y_B$  and  $1-y_B$  respectively. We consider a hexagonal lattice for this study. We have taken the lattice size  $L=256$ . It is observed that an increase in the lattice size changes the critical values slightly but the overall qualitative nature of the phase diagram is not affected [6, 9]. The periodic boundary conditions are employed and the simulation starts with a clean surface. The six nearest neighbouring (nn) sites of a selected site S are shown in figure 1. The only variable in our simulation is the feed concentration of  $B_3$ . The equilibrium coverages are measured as a function of  $y_B$ . In order to locate the critical points, ten independent runs each upto 50,000 Monte Carlo (MC) cycles are carried out. If ten runs proceed up to 50,000 MC cycles without the lattice being poisoned, then the particular point is considered to be in SRS. The poisoning of even a single run is a sufficient criterion for considering the point 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 10,000 MC cycles are ignored and the system is allowed to run upto 50,000 MC cycles in order to draw the phase diagram. Monte Carlo simulation is a stochastic process and in order to get equilibrium state and to minimize the

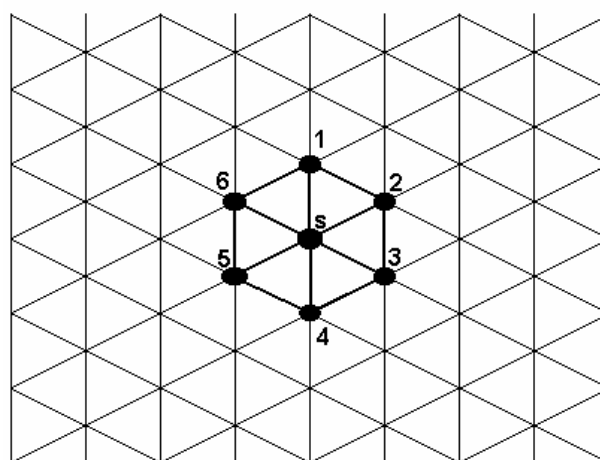


Figure 1. Six nearest neighbours of surface site S are marked as 1, 2, 3, 4, 5 and 6 respectively. See text for the detail.

error we need quite a few MC cycles. Moreover, if the system is allowed to run for more than 50,000 cycles no appreciable change in results takes place. In the initial 10,000 MC cycles the system is not in equilibrium and it retains equilibrium after 10,000 runs. Besides, since initially the lattice considered in the simulation is clean implying that no specie is present on the lattice, which is not the case in real circumstances, where the environmental gases get adsorbed in the lattice. So in order to imitate the real state of affairs, initial 10000 cycles have been ignored during which an adequate amount of reacting species adsorb in the lattice and perform reactions whenever it becomes possible such that the lattice corresponds to the real lattice as far as possible. The values of the coverage and the production rate are obtained after every 10 MC cycles, so that the final coverage (production rate) is an average of 4000 points.

Different steps involved in the simulation procedure are as follows: (a) A surface site (S) is chosen at random. If it is already occupied the trial ends, else the adsorption trial for  $A_3$  is made with probability  $1-y_B$ . For this purpose, three vacant sites are required. After random choice of a vacant site S, the second vacant site is picked randomly. The choice of the third vacant sites is also made at random in such a way that three vacant sites constitute the vertices of an equilateral triangle. If the second chosen site is marked as 1, then the two possible choices of an equilateral triangle are (1, 2, S) or (1, 6, S) as shown in Fig. 1. One of them is picked randomly. If the second chosen site is marked as 2, then the two possible choices of an equilateral triangle are (1, 2, S) or (2, 3, S) as shown in Fig. 1. One of them is picked randomly. Similarly, you can get another set of two possible choices of an equilateral triangle when the second chosen site is 3, 4, 5 or 6 respectively. One of the above-mentioned equilateral triangles is picked randomly in order to adsorb a trimer  $A_3$  in atomic form. However, it is important to note that the adsorption of a trimer on triplets of linear vacancies (1, S and 4), (2, S and 5) and (3, S and 6) is not allowed [6, 7]. (b) Adsorption of the trimer  $B_3$  is made in a similar way as that of the trimer  $A_3$  but with a probability  $y_B$ . (c) Atoms A and B sitting next to each other form AB that desorbs from the surface leaving behind two vacant sites. (d) In order to include the diffusion of B atoms in the above-mentioned reaction scheme one has to modify the step (b) of the simulation procedure. An adatom of the dissociated  $B_3$  molecule is selected

randomly. If the B adatom does not find an opposing specie for the reaction, its nearest neighbouring sites are checked randomly for an empty site. If an empty site is found the adatom is moved to that site while the previous site is vacated. If the randomly selected site is not empty then the trial ends. Another adatom of the  $B_3$  molecule is taken randomly and the possibility of diffusion is examined. Finally, the possibility of diffusion for the third adatom is considered. After a successful diffusion event, one has to investigate the nn sites for the presence of a reacting species as discussed in the earlier procedure. If any of the  $B_3$  molecule does not find a reacting specie then it's desorption is considered with the desorption probability P which varies from 0 to 1. It should be noted that diffusion of B atom is introduced with a maximum probability equal to one. Every  $B_3$  trimer which does not react on adsorption is desorbed from the surface with some probability P, leaving behind three vacant sites on the surface. The value of P varies from zero to one. If one of the atoms (B) of  $B_3$  trimer takes part in the reaction then desorption of  $B_3$  trimer is not considered [6, 11] even though the second B atom has another B atom in its nearest neighbourhood.

### 3. Results and Discussion

Without diffusion and desorption, the occurrence of a discontinuous transition point ( $y_C$ ) is observed at  $y_B = 0.50$  for TT model [10]. This single transition point separates one saturated state from another and is exactly related to the stoichiometry of this reaction. For  $y_B < y_C$ , the surface saturates with a combination of A atoms and randomly distributed isolated vacancies whereas for  $y_B > y_C$ , the surface saturates with a combination of B atoms and randomly distributed isolated vacancies. When we introduce the diffusion of B atoms in this system, the general features of the phase diagrams for the reaction scheme remain same as discussed above. The single transition point is precisely the same as for the reaction scheme without diffusion. However, for the saturated state above  $y_C$ , the coverage of B atoms gradually approaches to unity and finally becomes one. This behaviour is consistent with that observed in the dimer-dimer models of Khan et al. [6] and Albano [11].

However, the rate of desorption of one of the trimer species has a significant effect on the kinetics of the reaction. With zero desorption probability, the reaction is similar to the DD surface reaction of the type  $A_2+B_2 \rightarrow 2AB$  [6] which shows a

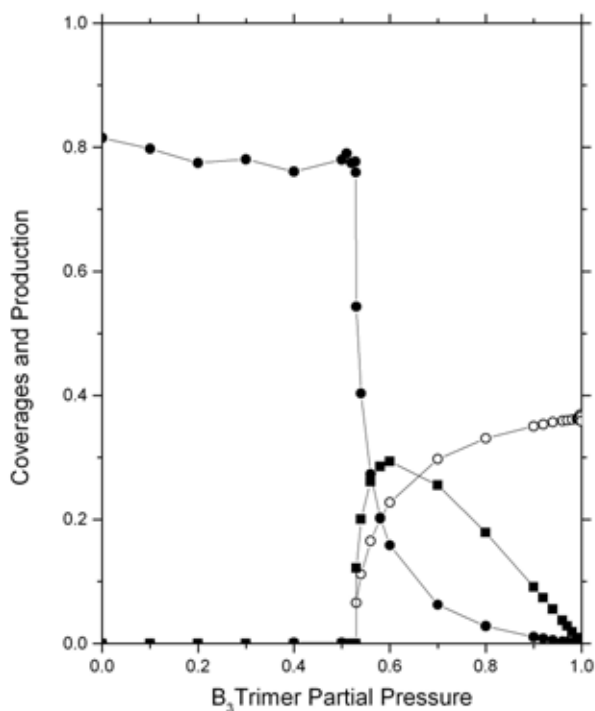


Figure 2. Coverages of trimers A (solid circle), B (open circle) and production AB (solid square) as a function of partial pressure for trimer-trimer model on a hexagonal lattice for desorption probability  $P=1.0$ .

discontinuous transition at  $y_B = 0.5$  (where  $y_B$  is the partial pressure of the  $B_2$  dimer). This system shows poisoning by A atoms for  $y_B < 0.5$  and poisoning by B atoms for  $y_B > 0.5$ . The saturation of the surface for  $y_B < 0.5$  ( $y_B > 0.5$ ) is due to a combination of A-atoms (B-atoms) and the isolated vacancies. The same features are reproduced for our TT model at  $P=0$ . At the other extreme with  $P=1$ , a continuous transition at  $y_B = 0.538$  separates a poisoned state from a reactive state. This reactive state continues for all values of  $y_B > 0.538$  as shown in Fig. 2. This situation is qualitatively similar to the one reported by Khan et al. [6] for the reaction  $A_2 + B_2 \rightarrow 2AB$  where they explore the effect of 100%  $B_2$  desorption. The situation becomes interesting as soon as  $P$  decreases from unity. In this case, a reactive state is obtained which is separated from an A + vacancies poisoned state by a continuous transition ( $y_1$ ) and a B + vacancies poisoned state by another continuous transition ( $y_2$ ). Figure 3 shows a typical phase diagram for  $P=0.90$ . For  $y_B < y_1$  ( $>y_2$ ), the surface is poisoned with A + 10% vacancies (B + vacancies). The phase diagram seems to resemble qualitatively with that of dimer trimer system [8]. The reactive window width is

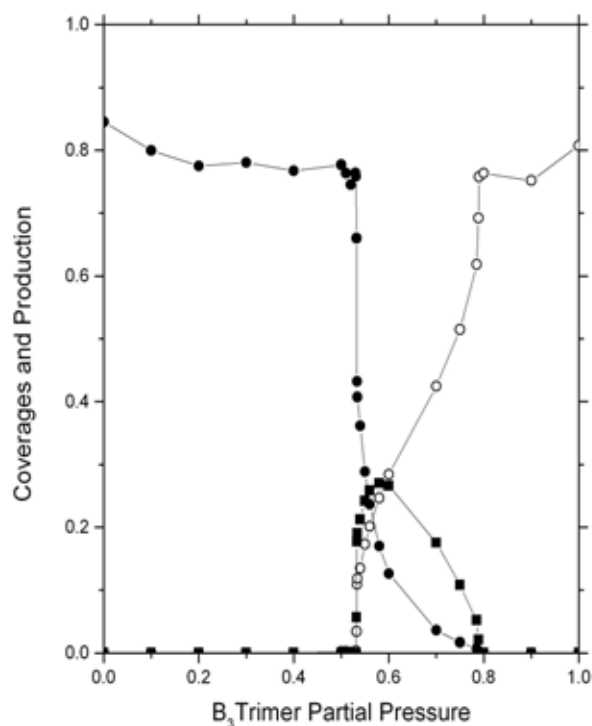


Figure 3. Coverages of trimers A (solid circle), B (open circle) and production AB (solid square) as a function of trimer partial pressure for trimer-trimer model on a hexagonal lattice for desorption probability  $P=0.90$

sensitive to the value of  $P$ . With decrease in  $P$ ,  $y_1$  remains almost constant whereas  $y_2$  shifts noticeably towards  $y_1$ . Figure 4 shows the variation of  $y_1$ ,  $y_2$  and the reactive window width  $w = y_2 - y_1$  as a function of  $P$ . At  $P \approx 0.1$ , the transition points merge, resulting in the disappearance of the reactive window. The width of the reactive window enclosed by  $y_1$  and  $y_2$  broadens as we increase  $P$  which is expected because by increasing the desorption probability of a specie we are increasing the vacant sites or the chance that an opposing specie could sit on the site for a reaction which enhances the reactive window. Broadening of this width shows an exponential behaviour with respect to  $P$  when the data is fitted. The dependence of  $w$  on  $P$  can be expressed by the relationship  $w = 0.00162 \exp(P/0.17685)$ . For  $P < 0.1$ , the behaviour of the model is same as for  $P = 0$  i.e. a single discontinuous point is observed separating the two poisoned states.

It has been observed that the continuous transition ( $y_1$ ) starts at some minimum value ( $\approx 0.1$ ) of  $P$  and an increase of  $P$  does not change the position of  $y_1$  significantly. Since each A atom requires one B atom in the nearest neighbourhood

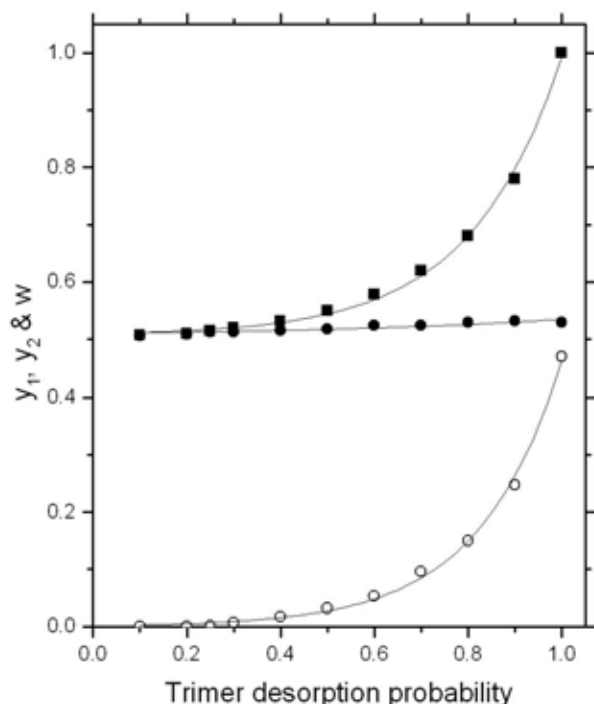


Figure 4. Transition points ( $y_1$  and  $y_2$ ) and reactive window width ( $w$ ) as a function of trimer desorption probability ( $P$ ) when diffusion and desorption of  $B_3$  are introduced in trimer-trimer model. Solid circle, solid square and open circle represent  $y_1$ ,  $y_2$  and  $w$  respectively.

for the continuous production of AB, this ratio can be maintained only if the adsorption rate of  $A_3$  trimer is high enough to utilize B atoms. The desorption of  $B_3$  trimer provides the empty surface sites where new adsorption events may take place which enhance the  $A_3$  adsorption rate for some minimum value of  $P$ . For this particular system, the required  $B_3$  desorption rate to produce SRS is obtained at  $P = 0.1$ . However, with increase in  $P$ ,  $y_2$  shifts towards the higher value of the feed concentration  $y_B$ . This is because an increase in  $P$  enhances the relative  $A_3$  impinging rate by providing more active sites through  $B_3$  desorption. For  $P = 1.0$  we have a special case. Once a  $B_3$  trimer adsorbs on the surface then there are two possibilities; it will react with  $A_3$  or it will desorb from the surface. In both cases, two or more vacant sites are produced with each  $B_3$  adsorption. This increases the  $A_3$  adsorption rate significantly

and even at  $y_B = 0.99$  we get sufficient amount of  $A_3$  to continue the particular reaction.

#### 4. Conclusion

For  $P = 0$  in trimer-trimer model, the behaviour is qualitatively similar to the DD reaction system [6] which shows a discontinuous transition at  $y_B = 0.5$ . For  $P = 1$  the behaviour is again qualitatively similar to the DD reaction system with  $B_2$  desorption [6]. For  $0.1 < P < 1$ , the behaviour resembles qualitatively the ZGB model with the difference that in our model the transition at  $y_2$  is continuous rather than discontinuous for ZGB model. The width of the reactive window enclosed by two transition points broadens as we increase  $P$ ; broadening of this width shows power law behaviour. This means that desorption of the trimer in trimer-trimer reaction systems plays the same role in enlarging the window width exponentially as played by desorption of the dimer in the dimer-dimer reaction model.

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