Kinetics of a dimer-dimer catalytic surface reaction type $AB+C_2$ to $1/2\ A_2+C_2B$

Kinetics of a dimer–dimer catalytic surface reaction of the type $AB + C_2 \rightarrow \frac{1}{2}A_2 + C_2B$

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Abstract. Dimer–dimer catalytic surface reaction of the type $AB + C_2 \rightarrow \frac{1}{2}A_2 + C_2B$ is studied by Monte Carlo simulation both on square and hexagonal lattices. Various models are proposed and studied. For the case of a square lattice the three models in which we (i) ignore both the diffusion and desorption of various reactants (M1 model), (ii) consider diffusion of C species only (M2 model), and (iii) consider the diffusion of C atoms as well as their recombination and desorption (M3 Model), all give a final poisoned state for all feed concentrations. For model M1 there is a continuous crossover from one poisoned state to another, while for M2 and M3 an irreversible phase transition separates one poisoned state from the other. The diffusion of A atoms (M4 model) is found to be very crucial to the evolution of the system towards a final steady reactive state. The slightest movement of the A atoms releases the trapped vacancies and other reactants which are available for further reaction. An irreversible phase transition now separates a poisoned state from a steady reactive state. For the hexagonal lattice the M3 model already leads the system towards a steady reactive state. The role of increasing the number of nearest neighbouring sites is seen to be similar to that of the diffusion of A atoms.

1. Introduction

The use of precious metals (Rh, Pd and Pt) as catalysts in the exhaust of automobiles to eliminate the emission of poisonous gases like NO, CO, N_2O, etc, has in recent years led to a spate in activity to understand better the mechanism behind the processes taking place on the surface of these metals. The presence of microscopic fluctuations and correlations in the concentrations of reactants makes the mean field theories ineffective. On the other hand lattice models have successfully accounted for a large range of these reactions. Depending on the type of reactants involved these reaction models are classified as of the type monomer–monomer (m–m), monomer–dimer (m–d), dimer–dimer (d–d), dimer–trimer (d–t) etc.

The m–m reaction model involves the hypothetical reaction $A + B \rightarrow AB$. The surface is modelled by a two-dimensional lattice. A (B) is adsorbed onto a randomly selected site with probability $p(1-p)$, which is proportional to the feed concentration of A (B). In case A and B happen to sit next to one another the product AB is formed which desorbs leaving behind two empty sites. This model has a steady reactive state (SRS) only for $p = \frac{1}{2}$, for all other values of p the lattice is poisoned either by A or by B

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reactant [1–4]. The m–d reaction model of the type $A + \frac{1}{2}B_2 \rightarrow AB$ was first studied by Ziff *et al* [5] and is commonly called the ZGB model. This model mimics the oxidation of CO (A denotes CO and B_2 denotes O_2). The B_2 molecule dissociates on adsorption, the two dissociated atoms are accommodated on adjacent sites. This model exhibits two irreversible phase transition (IPTS) points between which the system remains in SRS. The width of this reaction window depends on the type of lattice [6]. Another variant of the m–d reaction model is the reaction of the type $A + BC \rightarrow AB + \frac{1}{2}C_2$ [7–9]. It is found that this model exhibits the two IPTS and a SRS for a hexagonal lattice (each lattice site has six nearest neighbouring sites: in the literature this lattice has also been referred to as a triangular lattice) but not for the square lattice.

More recently Albano *et al* [10, 11] have studied the d–d reaction model of the type $\frac{1}{2}A_2 + B_2 \rightarrow AB_2$. They consider various variants of this model. They observe a SRS only when one of the species is allowed to diffuse and desorb. The d–t reaction $\frac{1}{2}A_2 + \frac{1}{3}B_3 \rightarrow AB$ has been studied by Kohler *et al* [12]. They observe two IPTS and a SRS for a hexagonal lattice.

In this paper we report results on a d–d reaction which differs from that studied by Albano *et al*. While they were interested in simulating the formation of H_2O through the reaction of H_2 and O_2 we would like to study the d–d reaction where NO reacts with H_2 to form N_2 and H_2O [13]. This reaction is one of the important processes that occur on the surface of a catalyst used in automobile exhausts. For the sake of generality we henceforth denote the two reacting molecules by AB and C_2. The reacton $AB + C_2 \rightarrow \frac{1}{2}A_2 + C_2B$ is studied both on a square lattice and a hexagonal lattice. The idea is to highlight the importance of the role of various processes taking place on the surface as well as the importance of the nature of the lattice in the promotion of the SRS. In the next section we discuss the model and the simulation procedure. We then present our results. The conclusions are presented in the final section.

2. Model and simulation

The d–d reaction mechanism proceeds according to the following Langmuir–Hinshelwood (LH) mechanism:

$$AB(g) + 2S \rightarrow A^S + B^S \tag{1}$$

$$C_2(g) + 2S \rightarrow 2C^S \tag{2}$$

$$A^S + A^S \rightarrow A_2(g) + 2S \tag{3}$$

$$B^S + C^S \rightarrow BC^S + S \tag{4}$$

$$B^S + BC^S \rightarrow C_2B(g) + 2S \tag{5}$$

where S denotes an active surface site, A^S an A atom adsorbed at a site S and (g) refers to the gaseous state. We consider four variants of the above reaction mechanism. In the simplest model (M1), the recombination and consequent desorption of C_2 is ignored. The diffusion of different reactants on the surface is also not taken into account. In the next model (M2) we assume diffusion of the lighter C atoms on the surface. We then introduce the desorption of C_2 as well as the diffusion of C on the surface (model M3). Finally in model M4 we impose the diffusion of a second species i.e. A or B on the model M3. As we will see, for a square lattice the first three models

do not lead to a SRS for any feed concentrations of the reactants. However, the introduction of a slight mobility of A atoms seems to be very crucial towards the evolution of the system towards a SRS. For a hexagonal lattice however the model M3 already leads the system towards a SRS.

The simulation of the model is performed on a square lattice of linear dimension $L = 40$ and on a hexagonal lattice with $L = 56$ (this value of L gives 1568 lattice sites which is roughly equivalent to the 1600 sites we have for the square lattice). Periodic boundary conditions are employed. A surface site is chosen at random. If it is already occupied the trial ends. Otherwise a neighbouring site is also selected randomly. If the neighbouring site is occupied the trial ends. If both sites are empty we choose C_2 or AB according to a probability p or $(1 - p)$, respectively. The molecules are adsorbed on the two sites in their atomic form. The nearest neighbours of each of the adsorbed atoms are scanned randomly for the possibility of the reactions described in equations (1–5). In model M1 an A sitting next to another A forms A_2 which desorbs from the surface leaving behind two empty sites. C atom sitting next to a B atom forms BC, C vacates its position and moves to the position of B. BC can again react with another nearest neighbour C atom to form C_2B which desorbs leaving behind two empty sites. Conversely a B sitting next to a C will form a BC at the position of B atom. Since B cannot have another C atom next to it, this reaction stops.

The diffusion (model M2) is simulated in the following way: if the initial selection leads to a site that is already occupied by C, then a nearest neighbour of C is picked up randomly. If this happens to be empty, C moves to this position. The neighbours of C are again checked for the possibility of further reaction of C as already described. If both B and BC are present in the neighbourhood of C, the choice of the formation of BC or C_2B is made randomly with equal probability. In model M3, if the adsorption of C_2 does not result in any reaction then C_2 is desorbed. However, if the diffusion of a C atom results in two C atoms sitting next to one another then the formation of C_2 is not allowed. Finally in model M4 we introduce the diffusion of a second species in addition to that of C. This model then assumes the desorption of C_2, diffusion of C and the diffusion of either B or A species. In the simulation the concentration of C_2 (p) is changed with a step of 0.1 or 0.05 except near the transition where the step size is reduced to 0.01.

Results and discussion

3.1. Square lattice

In figure 1(*a*) we show the coverages of various species Θ_A, Θ_B, Θ_C and Θ_{BC} as a function of the feed concentration p of C_2 for the model M1. For zero feed concentration the surface is covered by a combination of A and B atoms. Since A can recombine to form A_2 its starting coverage is less than that of B. The total coverage adds to almost 0.9. There are about 10% single empty sites distributed randomly on the surface. With an increase in p, Θ_A remains almost constant up to $p = 0.45 \pm 0.01$, beyond which it decreases uniformly to zero for $p = 1.0$. On the other hand Θ_B decreases while Θ_C increases with the increase in p. Both these trends become more pronounced in the vicinity of $p = 0.45$. Θ_{BC} which increases continuously up to $p = 0.45$, gradually drops to zero at $p = 1$. The total coverage shows a minimum of about 0.83 at $p = 0.50 \pm 0.01$. At $p = 1$ the surface is only covered with C atoms with trapped isolated vacancies. The coverage of 0.907 is consistent with a random
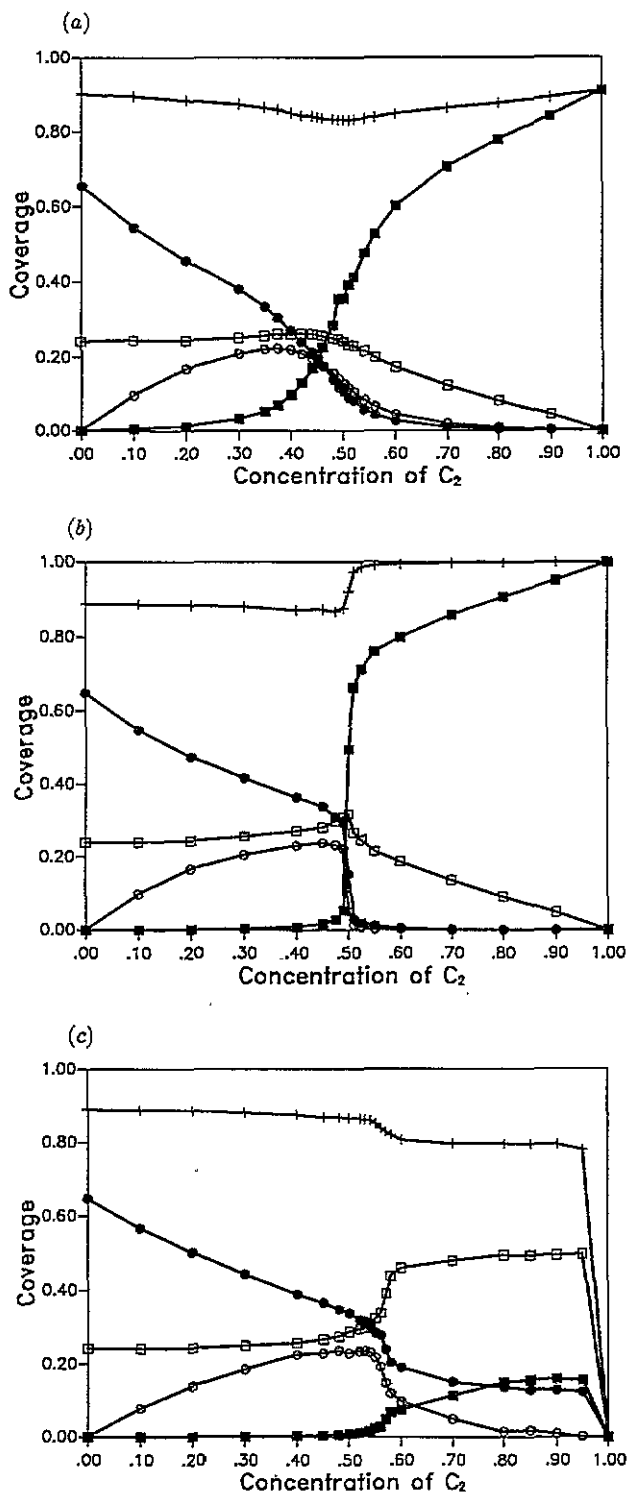
Figure 1. Coverages of A ($\square$), B ($\bullet$), C ($\blacksquare$), BC ($\bigcirc$) and total ($+$) as a function of the concentration of C_2 for model M1 (a), M2 (b) and M3 (c) for a square lattice.

distribution of dimers on a square lattice. For the entire range of C_2 concentration the steady state is a poisoned one with a continuous transition from a lattice poisoned by a majority of C atoms to a lattice poisoned predominately by other atoms. The crossover for which $\Theta_C \geqslant \Theta_A + \Theta_B$ occurs at $p = 0.50 \pm 0.01$.

With the introduction of diffusion of C atoms (Model M2), the general features of the phase diagram remain the same as for Model M1 (figure 1(b)). A pronounced transition is now observed at $p = 0.50 \pm 0.01$. The total converge beyond the transition becomes exactly one. This is understandable, since the diffusion of C atoms helps in eliminating the trapped isolated vacancies. The shift of transition point to $p = 0.50 \pm 0.01$ and the sharpness of the transition suggests a strong similarity of this model to the d–d reaction of the type $A_2 + B_2 \rightarrow 2AB$ which also exhibits an IPT from one poisoned state to another. The decrease in the diffusion rate of the C atoms does not have any quantitative effect on the results, except that the final equilibrium state is achieved after a longer time.

The introduction of desorption of the C_2 shifts the transition further to the right ($p = 0.54 \pm 0.01$) and also makes it less pronounced (figure 1(c)). For $p > 0.54$ C coverage does not show the same increase as for models M1 and M2. The A coverage on the other hand shows an upward trend. The total coverage which became one beyond the transition point for M2 model falls slightly below 0.8. The appearance of more vacancies sustains the reaction for a considerably longer time but the final equilibrium state is always a poisoned state. A final poisoned configuration of the system is reproduced in figure 2 for $p = 0.8$. It is observed that the A atoms tend to occupy alternate sites on the lattice. This traps the vacancies, the B atoms, the C atoms and the BC molecules which are no longer available for further reaction. It would thus appear that the positions occupied by the A atoms are extremely important for the production of a SRS.
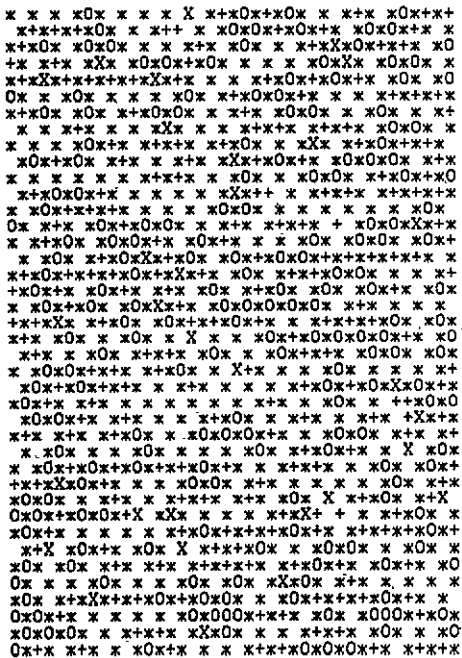
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Figure 2. A typical equilibrium configuration for the model M3 (square lattice) at $p = 0.8$. Vacancies are represented by blank sites, $*$, $+$, $\bigcirc$ and X denote the A, B, C and BC reactants respectively.
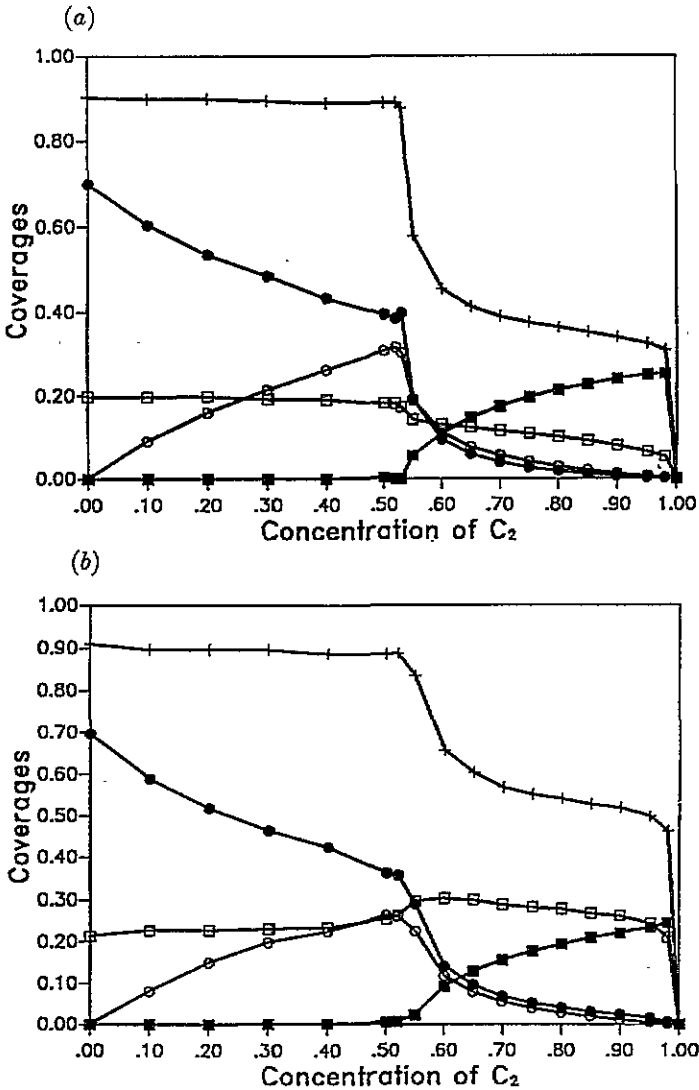
(a)

(b)

Figure 3. Same as figure 1, for model M4; diffusion probability $D_A = 1.0$ (a) and 0.10 (b).

In order to see the influence of the position of the A atoms we introduced diffusion of these atoms in the Model M4. The M4 model then consists in the imposition of the diffusion of A atoms on the M3 model. We introduce a diffusion probability for the A atoms which we call D_A. If the selection of a site results in picking up a site occupied by an A atom then this atom is moved to a neighbouring empty site (which is also picked up randomly) with a probability D_A. The phase diagram for the case $D_A = 1.0$ is reproduced in figure 3(a). An IPT is now observed at $p = 0.54 \pm 0.01$ beyond which the system exhibits a SRS. The C coverage and consequently the total coverge remain small beyond the transition point. This results in large clusters of empty sites which helps in the indefinite continuation of the reaction. The decrease in D_A does not significantly effect the overall picture. The C coverage and the total coverage increase slightly (beyond $p = 0.54$) but the system remains in SRS. Even for as small a value as

$D_A=0.001$ the system remains in SRS. For comparison we reproduce the phase diagram of the system for $D_A=0.001$ along with that of $D_A=1.0$ (figures 3(a) and 3(b), respectively). The production rates of A_2 and C_2B for different values of D_A are shown in figures 4(a) and (b). In each case there seems to be a broad peak for which the production rates remain maximum. To locate more precisely the position of the maximum production rate we studied this for $D_A=1.0$ in the range $0.60<p<0.65$ with a finer step of 0.01. In spite of the decrease in step size it is still not possible to determine the value of concentration which gives the maximum production rate. Within the statistical errors of our results the production rate remains maximum for C_2 concentration lying between 0.60 ± 0.01 and 0.65 ± 0.01. For lower values of D_A this peak broadens further, the maximum production rate starting at about the same value
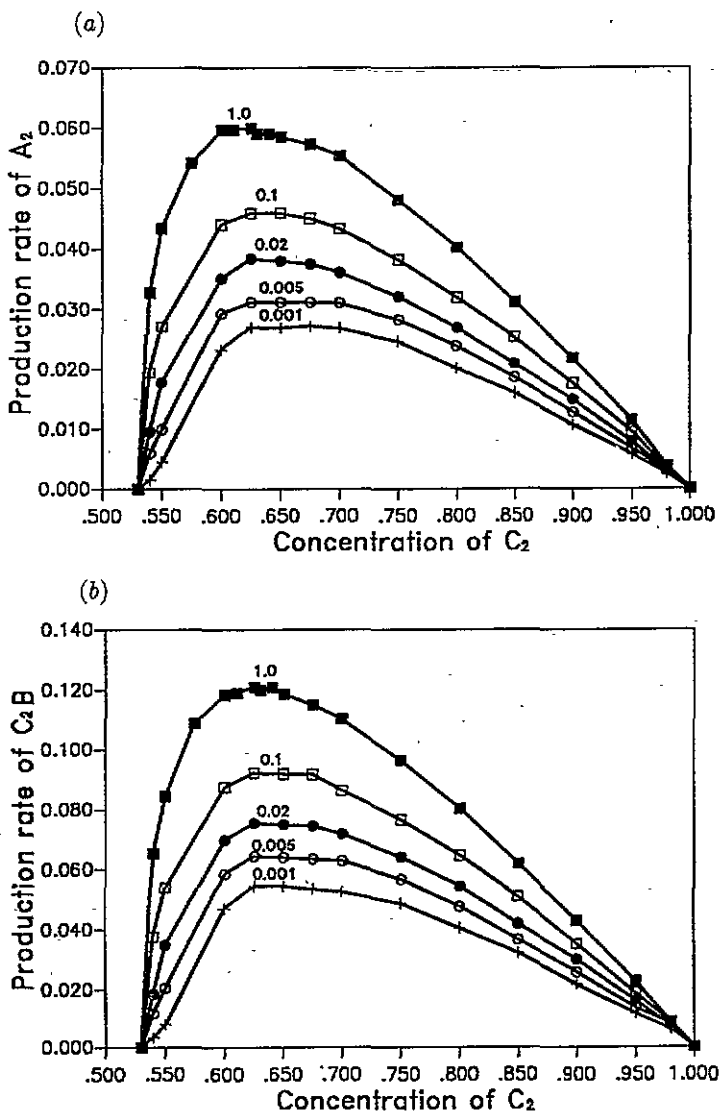

Figure 4. Production rates of A_2 (a) and C_2B (b) as a function of concentration of C_2 for different diffusion probabilities of A.
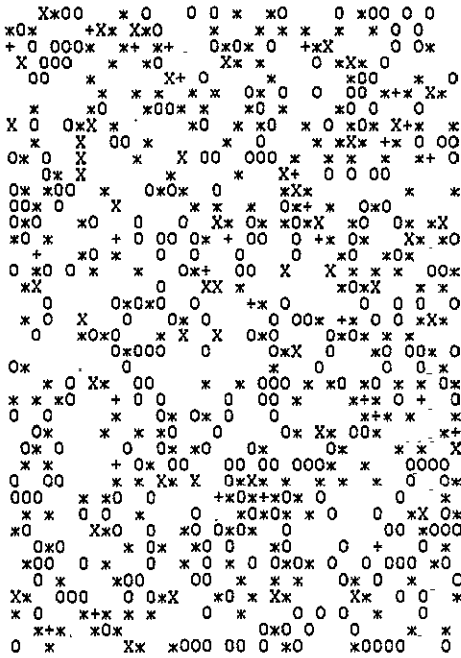
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of C_2 concentration in each case but ending at slightly higher values. An equilibrium configuration of the system at $p = 0.8$ and $D_A = 0.1$ is shown in figure 5. We can now clearly decipher clusters of vacancies which are essential for the maintenance of a SRS.

For a fixed concentration of C the production rates of both A_2 and C_2B increase with D_A according to a power law of the form:

$$R_x \sim D_A^{\beta_x} \tag{6}$$

where x stands for A_2 or C_2B. In figure 6 we plot D_A versus the production rate on a log–log plot to demonstrate this power law behaviour. The exponent β_x is the same for both the species and has a value 0.26 ± 0.01.

Finally we replace the diffusion of A atoms by that of B atoms. The picture now is similar to that of the M3 model. We do not observe a SRS for the entire range of C_2 concentration.

3.2. Hexagonal lattice

The coverages of the various species as a function of the concentration of C_2 for the models M1 and M2 are reproduced in figures 7(a) and 7(b), respectively. Qualitatively the results are the same as for the corresponding models in the case of a square lattice. The IPT from one poisoned state to the other takes place at 0.5 ± 0.01 for both the models, and is much sharper than the case of a square lattice. For the M3 model the effect of increasing the number of nearest neighbour sites is quite dramatic. A SRS is now observed for $0.5 < p < 1.0$ with an IPT again at $p = 0.5 \pm 0.01$ (figure 7(c)). The coverage of C atoms and consequently the total coverage remains depressed beyond $p = 0.5$. As for the square lattice this results in the formation of large vacancy clusters
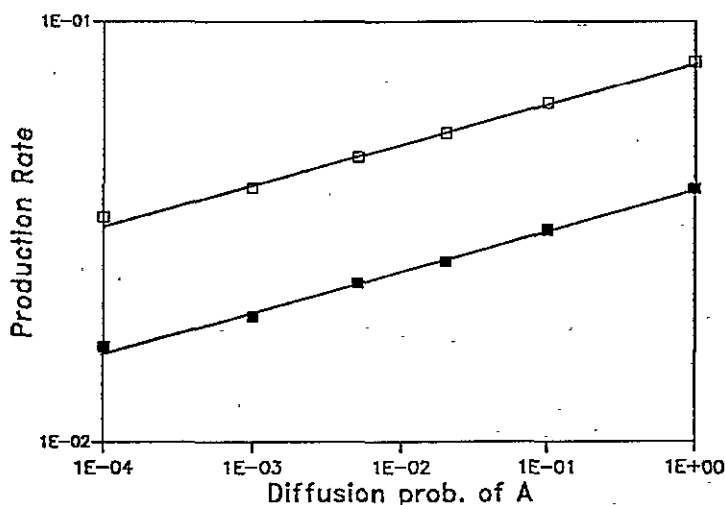
Figure 6. Production rates of C_2B (□) and A_2 (■) as a function of diffusion probability of A at $p = 0.8$ for a square lattice plotted on a log–log scale.

which helps keep the system in srs. The M3 model for the hexagonal lattice behaves in the same way as the M4 model for the square lattice. The effect of increasing the number of sites is the same as that produced by the diffusion of A atoms. In both cases the blockage produced by the entrapment of isolated vacancies and other species by the A atoms is removed.

Finally in figure 8 we reproduced the production rates of C_2B and A_2 for the hexagonal lattice. The trend shown by the production rates is similar to that observed for the square lattice. The maximum production rate is now observed for a range of C_2 concentration lying between 0.57 ± 0.01 and 0.65 ± 0.01. The production rates are slightly higher for the hexagonal lattice. The model M4 in the case of the hexagonal lattice does not change the qualitative picture of the M3 model it merely reinforces the production rates of the two gases.

Since the aim of the present study was to show the importance of diffusion and desorption on the eventual evolution of the system towards a srs we did not undertake a systematic study of the finite size effects. It has been shown in previous studies on catalytic surface reactions [6, 9, 10] that the size of the lattice does not change the overall qualitative picture, it only effects slightly the position of the ipt in passing from a poisoned state to a srs. The precise determination of these critical transition points is of importance in the determination of the critical exponents.

4. Conclusions

The observance of a srs in a system can depend on various factors. For the d–d reaction of the type $\frac{1}{2}A_2 + B_2 \rightarrow AB_2$ it was seen that the desorption of the B atoms plays a crucial role in leading the system from a poisoned state to a SRS [7, 8]. For the m–d reaction of the type $AB + C \rightarrow \frac{1}{2}A_2 + BC$ it was reported that the type of lattice is crucial for the sustenance of a continuous reaction [6]. A square lattice does not support a srs while a hexagonal lattice gives a window for srs.
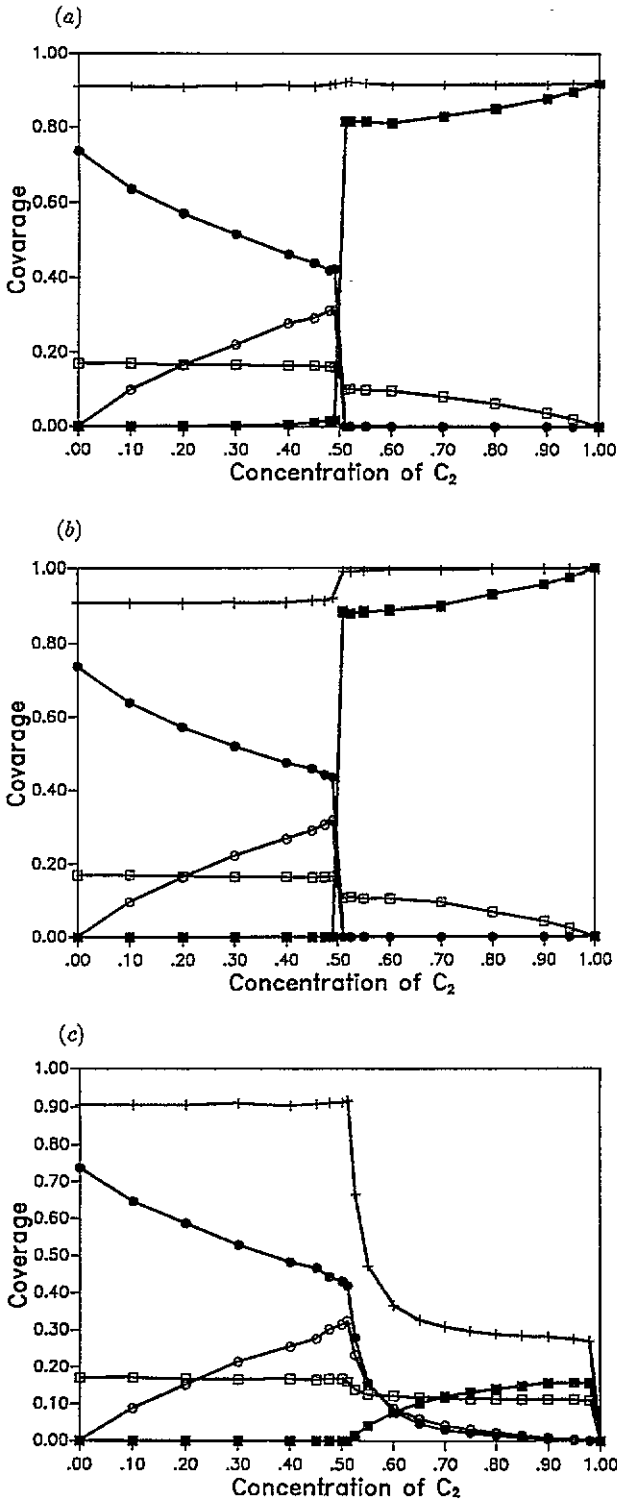
Figure 7. Coverages of A ($\square$), B ($\bullet$), C ($\blacksquare$), BC ($\bigcirc$) and total ($+$) as a function of the concentration of C_2 model M1 (a), M2 (b) and M3 (c) for a hexagonal lattice.
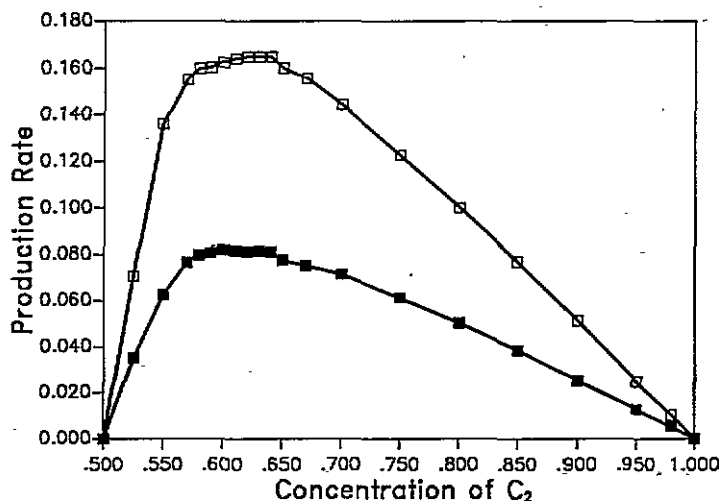
Figure 8. Production rates of C_2B (■) and A_2 (□) as a function of the concentration of C_2 for a hexagonal lattice.

It is clear that for the catalytic surface reaction of the type $AB + C_2 \rightarrow \frac{1}{2}A_2 + C_2B$ that both the diffusion of the A atoms and the nature of the lattice are extremely important for the observance of a SRS. For a square lattice a SRS is obtained with a combination of (i) diffusion of C (ii) desorption of C_2 and (iii) a very slight movement of the A atoms. For the hexagonal lattice the first two conditions are sufficient to generate a SRS. The increase in the number of nearest neighbours plays the same role as that played by the movement of A atoms for the square lattice. It is suggested that the role of diffusion and desorption of various adsorbed species as well as the effect of the nature of the lattice be carefully analysed for the previously studied catalytic reactions where no reaction window was observed.

Acknowledgments

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