NO-CO catalytic reaction on a square lattice: the effect of the Eley-Rideal mechanism

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Abstract
Monte Carlo simulations have been used to explore the effects of the Eley–Rideal mechanism (reaction of CO molecule with already chemisorbed oxygen atom to produce CO_2) on a simple Langmuir–Hinshelwood model for the NO–CO catalytic reaction on a square surface. The diffusion of the CO and N adatoms on the surface and desorption of CO from the surface are also introduced into the model. Without diffusion and desorption, the model generates a very small reactive window of the order of 0.033. The moment CO partial pressure (y_{CO}) departs from zero, continuous production of CO_2 and N_2 starts. A first-order transition terminates the catalytic activity at $y_{CO} = 0.033$ and the surface is poisoned with a combination of CO and N. However, the diffusion of the N atom and CO molecule shifts the transition point from 0.033 to higher values of y_{CO}. The introduction of desorption of CO shows some interesting results. A very small desorption probability of CO (=0.01) increases the width of the reactive window to 0.12. However, this reactive window is separated by two transition points $y_1(\approx 0.2)$ and $y_2(\approx 0.32)$. For $y_{CO} < y_1$ ($y_{CO} > y_2$) the surface is poisoned by a combination of O and N (CO and N). With further increase in desorption probability the width increases significantly.

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1. Introduction

Together with the great importance of studies of the CO oxidation reaction, there has also been great interest in the reduction of NO by CO. Both reactions are important in automotive exhaust emission control. It was found that catalytic activity of Pt surfaces in the NO–CO reaction is correlated with their efficiency in dissociating NO, which varies between zero and 100% for different planes [1, 3]. Fink *et al* [2] have shown that NO adsorbs molecularly at room temperature and dissociates upon heating above ≈380 K. The dissociation rate of NO fluctuates around unity. Recently, von Tol and Nieuwenheys [3] have also shown that NO

adsorption takes place at 80 and 300 K with a very high sticking coefficient on all planes studied. However, NO dissociation takes place when the temperature is increased. This is because at higher temperature vacancies are created due to NO desorption. Molecular NO desorption takes place with a maximum rate around 400 K when saturated surfaces are heated [3]. At a typical operating temperature for a catalytic converter (700 K) the adsorption of NO results in the liberation of N_2 gas and in the formation of stable surface oxygen [4, 5].

Ever since the introduction of the Ziff–Gulari–Barshad (ZGB) lattice gas model [6] for the heterogeneously catalysed CO–O_2 reaction, the study of reactive processes using Monte Carlo (MC) simulation has undergone rapid growth [7–23]. Yaldram and Khan [7, 8] applied the ZGB model to the NO–CO surface reaction on square and hexagonal (triangular) lattices. They showed that the type of lattice and the dissociation rate of NO (r_{NO}) into N and O are important factors for this reaction system. For a square lattice, they observed a poisoned state for all values of r_{NO} and feed concentration of CO (y_{CO}). However, a steady production of N_2 and CO_2 is observed for a hexagonal lattice when $r_{NO} > 0.80$. For $r_{NO} < 0.8$, no reactive window is obtained even for a hexagonal lattice, where the reactive window is defined as the region in which the steady production of N_2 and CO_2 takes place. A maximum window width (≈ 0.153) is obtained at $r_{NO} = 1.0$ (i.e. complete dissociation of NO). This reactive window is enclosed by second-order phase transition (SOPT) and first-order phase transition (FOPT). An SOPT is observed at $y_2 = 0.185$ whereas an FOPT is observed at $y_1 = 0.338$. Yaldram and Khan [7, 8] have referred to this particular case of $r_{NO} = 1.0$ as the simple Langmuir–Hinshelwood (LH) mechanism for the NO–CO reaction system. Under the conditions mentioned above, the simple LH mechanism (in which NO adsorbs in dissociated form) of Yaldram and Khan [7, 8] is of great interest at the operating temperature of a catalytic converter. A number of authors have used this simple mechanism to study different aspects of this reaction system [13–22].

Meng *et al* [16] used the simple LH mechanism for this reaction system. They added a side-reaction channel according to which nearest-neighbouring pairs of CO–N combine to form CON, which desorbs, leaving behind two vacant sites on the surface. They showed that, adding a new reaction channel in order to decrease the possibility of poisoning, one might enhance the reactivity of this system. For simulations on the square lattice, the addition of the side reaction channel causes the opening of a reaction window with SOPT close to $y_{CO} \approx 0.262$ and FOPT close to $y_{CO} \approx 0.501$. Khan *et al* [20] introduced the diffusion of the species in the simple LH mechanism for this reaction system. They have shown that only the diffusion of N atoms on the surface brings the system into a reactive state. For maximum diffusion probability ($P = 1$), they obtained a reactive window of the order of ≈ 0.10. Recently, Dickman *et al* [19] also showed theoretically that surface diffusion of nitrogen can only lead to an active state on a square lattice for this reaction system. Khan [21] and Ahmad and Khan [22] have also used this simple model to examine the influence of the subsurface oxygen in the reaction system. The introduction of subsurface oxygen produced some very interesting results.

When NO adsorbs on two sites, it is equally likely that one of the sites is filled with an N atom and one by an O atom, and this simple fact leads inevitably to poisoning on a square lattice by a process of 'chequerboarding' of N atoms [13]. However, on a hexagonal lattice this chequerboarding process cannot occur geometrically and, therefore, we obtain a steady reactive region on that surface [7, 21]. Meng *et al* [16] have broken this chequerboarding process by introducing a hypothetical reaction between CO and N. Khan *et al* [20] have broken the chequerboarding process of N atoms by introducing diffusion of N atoms on the surface. Khan [21] has introduced one subsurface site in the usual four surface sites of a square lattice to break the chequerboarding process. More recently, Khan *et al* [23] have studied a simple ZGB-like lattice gas model for the reaction of CO and NO on a Na-modified square surface.
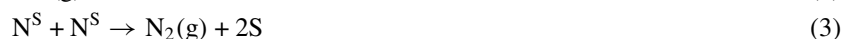
The Na-induced NO dissociation in the model also breaks the usual chequerboarding process of N atoms on the square surface.

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. One class of such catalysed reactions is imagined to proceed via the Eley–Rideal (ER) mechanism, in which a gas-phase reactant, never in equilibrium with the surface, directly picks up a fragment of the adsorbed reactant and forms a product that leaves the surface. This class of reaction, halfway between the gas-phase type and LH type, is of interest in surface science. Jackson and Persson [24] have studied the dynamics of a 'hot' hydrogen dimer in the ER process (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 [25] 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 continuous production of CO_2 starts. This production continues until $y_{CO} \approx 0.497$, where an FOPT terminates this activity and the surface is poisoned by CO. Using the ER process, Meakin has also studied a monomer–monomer reaction system and obtained similar results.

The objective of this paper is to explore the effects of the ER process on the phase diagram of the LH-type model for the NO–CO surface catalytic reaction system. In this study, we shall also study the effect of diffusion of the species and the desorption probability of CO on the phase diagram of the system. The paper is structured as follows: in the next section the reaction model and the simulation procedure are 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 model of the system can be written in the form of the following equations:

$$CO(g) + S \rightarrow CO^S \tag{1}$$
$$NO(g) + 2S \rightarrow N^S + O^S \tag{2}$$
$$N^S + N^S \rightarrow N_2(g) + 2S \tag{3}$$
$$CO^S + O^S \rightarrow CO_2(g) + 2S. \tag{4}$$

With the introduction of the ER process, one has to add the following equation:

$$CO(g) + O^S \rightarrow CO_2(g) + S \tag{5}$$

where S is an empty surface site, (g) refer to the gas phase and X^S represents an X adatom. There appears to be considerable uncertainty concerning the relative importance of LH and ER reaction steps, given by equations (4) and (5) respectively [25, 26]. It is worthwhile to mention that the relative frequency of the 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 the ER reaction step becomes dominant, otherwise the LH reaction step becomes important [26]. We have studied two different cases. In the first case we investigate the addition of reaction step (5) to the usual simple LH model of the reaction system. In the second case we eliminate adsorption step (1) and reaction step (4) so that it is a pure ER reaction on a pre-adsorbed oxygen surface.

We consider an infinite reservoir filled with CO and NO with partial pressures y_{CO} and $1 - y_{CO}$ respectively. This reservoir is in contact with a surface which is simulated by means of a square lattice of linear dimension $L = 128$. It is observed that an increase in the lattice size changes the critical pressures slightly but the overall qualitative nature of the phase diagram is

not affected [11, 27]. Periodic boundary conditions are used in order to avoid boundary effects. 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 MC cycles were carried out. If all the ten runs proceed up to 50 000 MC cycles without the lattice being poisoned, 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 obtain 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 ten MC cycles, so that the final coverage (production rate) is an average taken over 4000 configurations.

The CO or NO molecules are selected randomly with relative probabilities y_{CO} and $1 - y_{CO}$ respectively. The steps involved in the simulation are as follows: a surface site S is selected at random. (a) If CO happens to be the molecule selected, then one of the following events occurs. (i) If the randomly selected site is vacant then CO is adsorbed on it. The nn sites of the adsorbed CO are scanned for the presence of an O atom. If O atoms are found, one of them is randomly chosen to react with CO through reaction step (4) and the trial ends. No CO can sit next to O on the surface. If no O is found in this scan then the trial ends (because the reaction of CO with other species (N) is not possible in this scheme). (ii) If the randomly selected site S is occupied by O atom then CO directly reacts with it in order to complete ER step (5) and the trial ends. (b) If the selected molecule is NO and if the randomly selected site S is occupied, then the trial ends. If the randomly selected site S is vacant then the nn sites of S are scanned for the presence of a vacancy. If vacancies are found, one of them is randomly chosen to adsorb NO in atomic form through step (2). The nn sites of N^S and O^S atoms are then examined randomly (as discussed above) for the presence of N^S and CO^S in order to complete reaction steps (3) and (4), respectively. If all four nn sites of site S are occupied then the trial ends and a new molecule is selected. Therefore, our model (without diffusion and desorption) involves only one variable, i.e. partial pressure of CO (y_{CO}).

In order to introduce the diffusion of a particular species X^S, the simulation procedure is slightly modified. If the randomly selected site S is occupied by X^S species, then its four nn sites are scanned randomly (as discussed above) for the presence of a vacancy. The trial ends if a vacancy is not found in the neighbourhood. If a vacancy is found, the species X^S diffuses onto this new site and the site previously occupied by X^S is vacated. After diffusion, the event possibility of a particular reaction is examined in a similar way as discussed above. It should be noted that the diffusion probability of a particular species X^S is set to unity. With the introduction of diffusion of the species X^S, there is still only one variable, i.e. partial pressure of CO (y_{CO}). In order to incorporate desorption of the CO molecule, the simulation procedure is again slightly modified. If a CO molecule occupies the randomly selected site S, then it desorbs from the surface ($CO^S \rightarrow CO(g) + S$) with some probability (d_{CO}) leaving behind a vacant site and the trial ends. The probability d_{CO} varies from zero to one in a step of 0.1. Therefore, in this study there are two varying parameters involved, i.e. y_{CO} and d_{CO}.

3. Results and discussion

In the absence of reaction step (5), the numerical results are well known [7, 8]. A square lattice results in a final poisoned state for all feed concentrations of CO. With the introduction of equation (5), the situation changes. Figure 1 shows the phase diagram of the case when reaction step (5) is taken into account (along with the LH model). For $y_{CO} = 0$, the coverages of O (θ_O) and N (θ_N) are ≈ 0.65 and 0.25 respectively (random dimer filling). There are almost 10% isolated vacancies, which are randomly distributed on the surface. With the inclusion
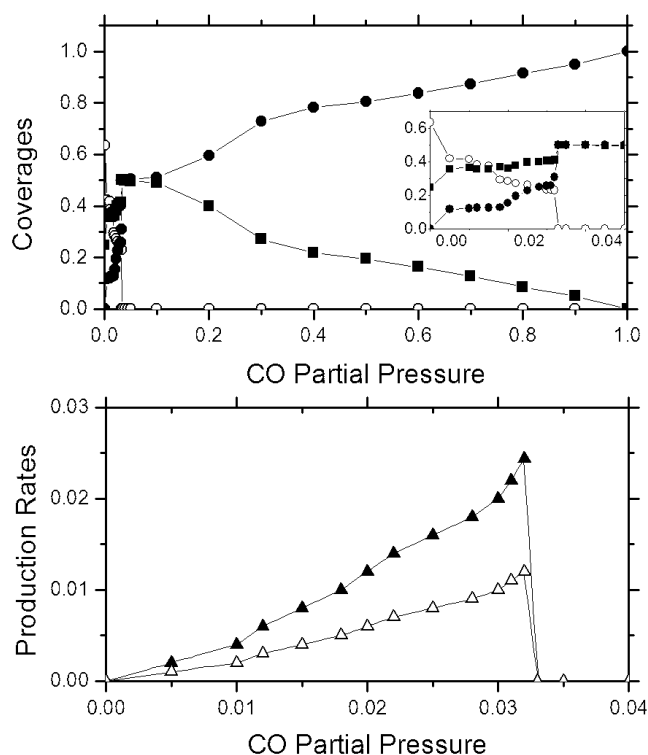
Figure 1. The coverages (top) of CO (solid circle), O (open circle) and N (square) versus CO partial pressure in the reservoir for the case when ER processes are added to the usual LH model of the system. The blown-up portion of the reactive region is shown in the inset. The production rates (bottom) of CO_2 (solid triangle) and N_2 (open triangle) are also shown.

of a very small amount of CO ($y_{CO} = 0.005$), the system enters the SRS with continuous production of CO_2 and N_2. θ_O drops to ≈ 0.42 whereas θ_N shoots to ≈ 0.36. The CO molecules with coverage (θ_{CO}) ≈ 0.11 are also trapped between N atoms and vacancies (figure 2). This trapping indicates that diffusion of either of the species can enhance the reactivity. The FOPT stops the catalytic activity at $y_{CO} = 0.033$ (± 0.001) and the surface is poisoned with a combination of CO and N atoms (figure 2). Here, the same chequerboarding of N atoms as seen in LH model on the square surface is reproduced.

In the LH model, for low CO (high NO) partial pressure, the surface contains clusters of oxygen with N atoms trapped in these clusters. In the present model, reaction step (5) (in the same region) on one hand burns the chemisorbed oxygen of these clusters whereas on the other hand it creates isolated vacancies inside these clusters. On these isolated vacancies the CO molecule is chemisorbed (the NO molecule cannot be chemisorbed because it requires a pair of vacancies), which triggers reaction step (4) too. In this way oxygen is being burnt very quickly. The generation of isolated vacancies (due to ER reaction step (5)) and occupation of N atoms (trapped between vacancies and non-reacting species) results in a decrease in pairs of vacancies. This reduces the chance of NO adsorption and thus CO begins sitting on the surface along with N atoms, and ultimately we observe a situation as shown in figure 2 (bottom). Experiments to distinguish reaction step (4) and reaction step (5) have been carried out with molecular beams impinging on the Pd surface [26, 28]. These experiments have shown that due to reaction step (5) the reactivity is very fast in the region of highest coverage

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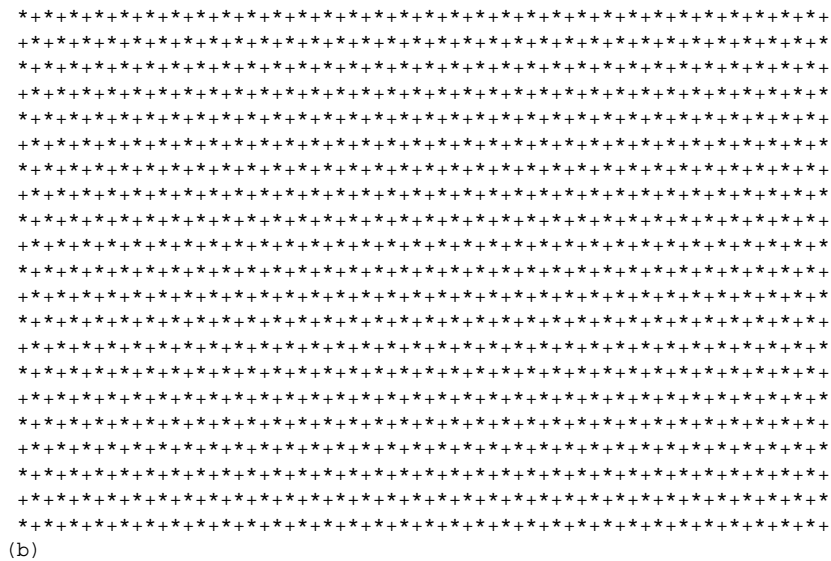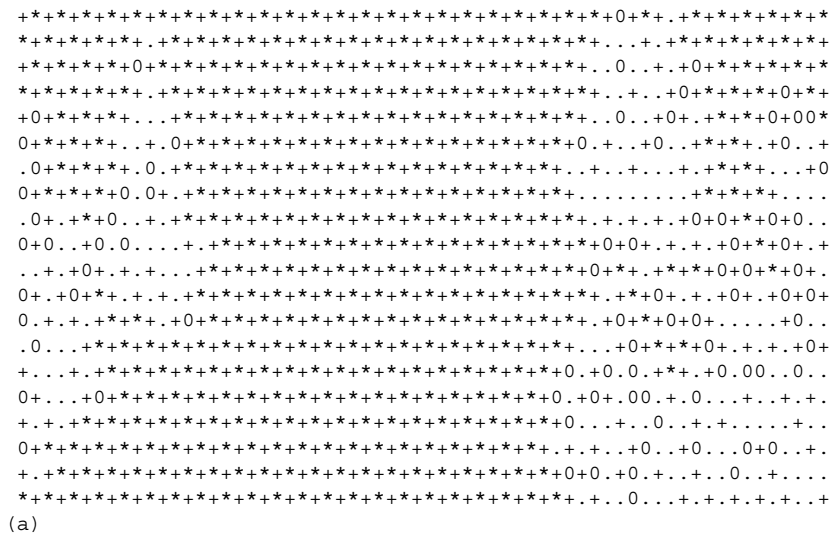
Figure 2. Surface snapshots of the reactive region ($y_{CO} = 0.01$) and poisoned state ($y_{CO} = 0.04$) are shown top and bottom respectively. The representation of the species is as follows: CO = '*', O = 'O', N = '+' and vacancy = '.'.

of adsorbed oxygen. The LH reaction treatment is effective when CO and O surface coverages are low. These experimental observations are consistent with our findings. The catalytic activity is very fast in a small steady reactive region. The burning rate of oxygen (despite the fact that the oxygen partial pressure is too high) is very high and only 3% CO partial pressure burns all the oxygen of the surface.

Figure 3 shows a phase diagram of the system when diffusion of CO is introduced into the model. The continuous production of CO_2 and N_2 starts the moment y_{CO} departs from zero. However, the value of the FOPT shifts to 0.020 ± 0.001. This is because with the introduction
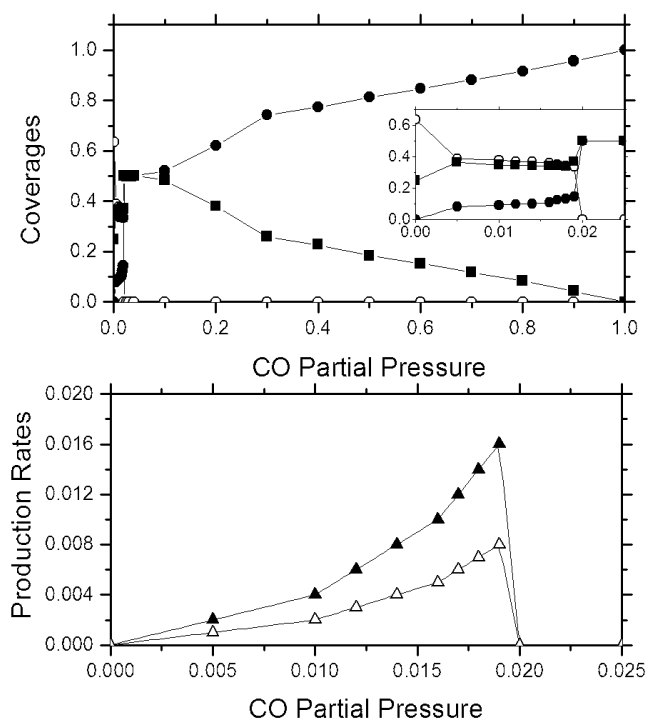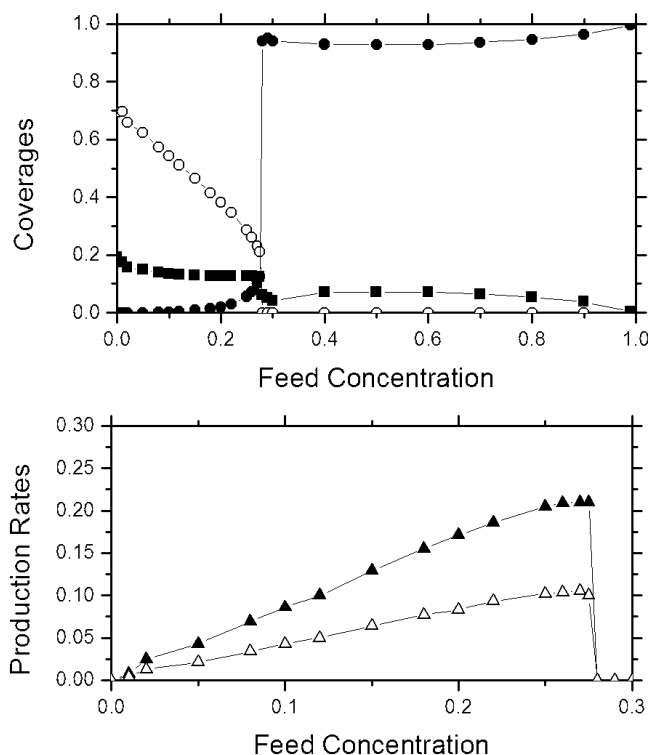
Figure 3. The same as in figure 1 for the case where CO diffusion is added to the model.

of diffusion, CO molecules are more quickly burnt. It is important to note that in the LH model the diffusion of the CO molecule has no effect on the phase diagram of the system. Figure 4 shows a phase diagram of the system when diffusion of N is introduced into the model. Here, again the continuous production of CO_2 and N_2 starts the moment y_{CO} departs from zero. However, in this case the value of FOPT shifts to 0.280 ± 0.005 respectively. This is an interesting result. In the LH model the diffusion of N atoms reveals a phase diagram which is qualitatively similar to the ZGB model (with continuous and discontinuous transition points and window width of the order of ≈ 0.10). However, in this particular case, not only is the continuous transition eliminated but also the width of the reactive region is significantly larger (≈ 3 times as large).

With the introduction of a very small probability of CO desorption ($d_{CO} \approx 0.01$) in the absence of diffusion of the X^S species, the situation significantly changes. When $d_{CO} = 0.01$, two transition points (y_2 and y_1) are observed at $y_{CO} = 0.20$ and 0.32 respectively. This shows that desorption of the CO molecule again brings the system into a situation which was seen in the LH model when N diffusion (equal to unity) was considered, where the two transition points were ≈ 0.20 and ≈ 0.30. For $y_{CO} < y_1$ ($y_{CO} > y_2$), the surface is poisoned by a combination of O and N (CO and N). Therefore, the reactive window width is of the order of 0.10. In fact this small desorption of CO increases the number of pairs of vacancies and hence the NO supply is increased (due to its high pressure and availability of pairs of vacancies). This poisons the surface until $y_{CO} > 0.20$, where some CO molecules start occupying the sites and activity starts again. With increase in d_{CO}, the values of y_2 and y_1 shift towards a higher value of y_{CO}. This situation is shown in figure 5. It is seen that initially the values of y_1 and y_2 increase rapidly with increase in d_{CO} and then increase is very slow. It is important to note that it has

Figure 4. The same as in figure 1 for the case where N diffusion is added to the model.

been mentioned previously that the generation of isolated vacancies due to the ER reaction step and occupation of N atoms (trapped between vacancies and non-reacting species) results in a decrease in the number of pairs of vacancies. This is because the ER reaction step burns oxygen atoms from the clusters of oxygen quickly, and when the oxygen starts depleting, the isolated vacancies are filled by CO itself (because NO cannot be adsorbed on a single site), which causes the chequerboard problem of N and CO as shown in figure 2. On the other hand, in this particular case, isolated vacancies generated by CO desorption enhance the number of pairs of vacancies, eliminating the chequerboard pattern (since NO is more likely to be adsorbed due to its higher partial pressure), which results in an SRS at $y_{CO} \approx 0.20$.

Figure 6 shows the situation when adsorption step (1) and reaction step (4) are eliminated (pure ER reaction) from the present model. This situation is qualitatively very similar to the situation shown in figure 1. However, here the reactive window width has almost been doubled. With the inclusion of a very small amount of CO ($y_{CO} = 0.005$), the system enters an SRS with continuous production of CO_2 and N_2. The FOPT stops the catalytic activity at $y_{CO} = 0.062(\pm 0.001)$. The surface is poisoned with a combination of isolated vacancies and N atoms forming a chequerboard pattern (as CO is not allowed to be adsorbed on the surface). The coverage of N and isolated vacancies is 0.5 each. On these vacancies NO cannot be adsorbed. However, diffusion of N may be useful. Figure 7 shows such an interesting situation. With the inclusion of a very small amount of CO ($y_{CO} = 0.005$), the system enters an SRS with continuous production of CO_2 and N_2. The production continues until a very small amount of NO concentration is present in the reservoir. The production is only stopped
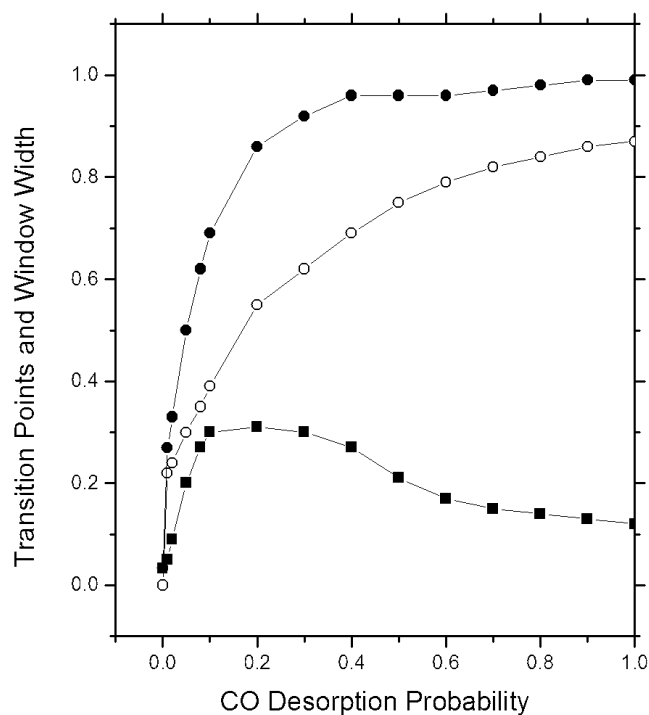
**Figure 5.** The transition points and reactive window width (w) as a function of CO desorption probability. The representations of y_1, y_2 and w are open circles, solid circles and squares, respectively.

when NO is completely switched off. Such behaviour has been shown by Meng *et al* [9] by taking the desorption probability of CO as equal to that of NO, which is 0.5.

In a real experimental situation, the productive activity strongly depends upon temperature. In our simulations the temperature is involved through desorption of CO molecules from the surface. We have seen that our model with the inclusion of diffusion of N atoms eliminates the usual SOPT (y_2) of the reaction system [7, 20]. The continuous production of CO_2 and N_2 starts the moment $y_{CO} \neq 0$. This observation is consistent with the theoretical [16, 21, 29] and experimental findings [2]. In the theoretical calculations, desorption of CO and NO was considered [16, 29] whereas in our model such desorption has been completely ignored. Khan [21] introduced the diffusion of oxygen to the subsurface in the usual model of Yaldram and Khan [7] in order to eliminate the SOPT.

4. Conclusions

MC simulations have been used to explore the effects of the ER mechanism (reaction of a CO molecule with an already chemisorbed O atom to produce CO_2) on a simple LH model for the NO–CO catalytic reaction on a square surface. The usual chequerboarding process of N atoms on the surface of a square lattice has been broken down. The moment CO partial pressure (y_{CO}) is unequal to zero, continuous production of CO_2 and N_2 starts and remains continuous up to $y_{CO} = 0.034$. Therefore, the width of the reactive window is very small. For $y_{CO} > 0.034$, the catalytic activity stops and the surface is poisoned with a combination of CO and N. Diffusion
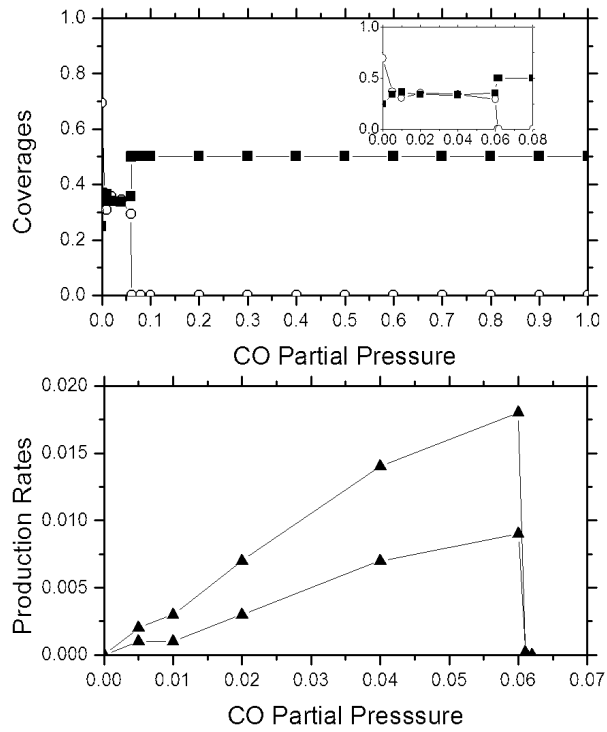
Figure 6. The same as in figure 1 for the case when adsorption step (1) and reaction step (4) are ignored in the model.
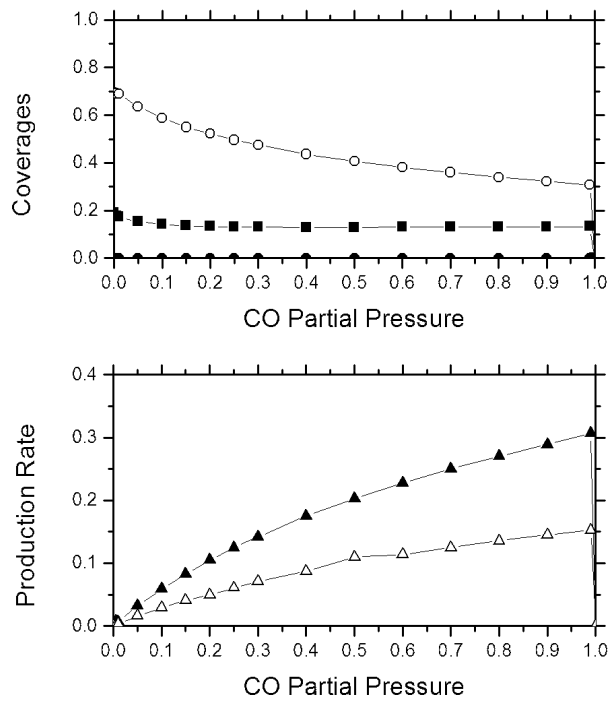
Figure 7. The same as in figure 6 when diffusion of N atoms is also considered.

of CO on the surface further reduces the width of the reactive region. However, diffusion of N atoms widens the reactive window width significantly. With the introduction of small CO desorption probability (≈ 0.01), the situation changes completely. The system reveals a phase diagram with two transition points ($y_1 \approx 0.20$ and $y_2 \approx 0.32$), which is qualitatively similar to the ZGB model (where $y_1 \approx 0.395$ and $y_2 \approx 0.525$). The width of the reactive window initially increases with increase in CO desorption probability and then attains an almost constant value.

References

[1] Banholzer W F, Park Y O, Makand K M and Masel R I 1983 *Surf. Sci.* **128** 176
[2] Fink Th, Dath J P, Bassett M R, Imbihl R and Ertl G 1991 *Surf. Sci.* **245** 96
[3] von Tol M F H and Nieuwenheys B E 1993 *Appl. Surf. Sci.* **67** 188
[4] Dubois L H and Somorjai G A 1980 *Surf. Sci.* **91** 414
[5] Hendershot R E and Hansen R S 1986 *J. Catal.* **98** 150
[6] Ziff R M, Gulari E and Barshad Y 1986 *Phys. Rev. Lett.* **56** 2553
[7] Yaldram K and Khan M A 1991 *J. Catal.* **131** 369
[8] Yaldram K and Khan M A 1992 *J. Catal.* **136** 279
[9] Meng B, Weinberg W H and Evans J W 1994 *J. Chem. Phys.* **101** 3234
[10] Khan K M, Yaldram K, Khalifeh J and Khan M A 1997 *J. Chem. Phys.* **106** 8890
[11] Khan K M, Yaldram K and Ahmad N 1998 *J. Chem. Phys.* **109** 5054
[12] Khan K M, Basit A and Yaldram K 2000 *J. Phys. A: Math. Gen.* **33** L315
[13] Brosilow B J and Ziff R M 1992 *J. Catal.* **136** 275
[14] Cortes J, Puschmann H and Valencia E 1998 *J. Chem. Phys.* **109** 6086
[15] Cortes J and Valencia E 1998 *Chem. Phys.* **229** 265
[16] Meng B, Wienberg W H and Evans J W 1993 *Phys. Rev. E* **48** 3577
[17] Cortes J, Puschmann H and Valencia E 1996 *J. Chem. Phys.* **105** 6026
[18] Yaldram K, Khan K M, Ahmad N and Khan M A 1993 *J. Phys. A: Math. Gen.* **26** L805
[19] Dickman A G, Grandi B C S, Figueiredo W and Dickman R 1999 *Phys. Rev. E* **59** 6361
[20] Khan M A, Yaldram K, Khalil G K and Khan K M 1994 *Phys. Rev. E* **50** 2156
[21] Khan K M 2000 *Surf. Sci.* **470** 155
[22] Ahmad N and Khan K M 2001 *Chem. Phys.* **263** 319
[23] Khan K M, Basit A and Albano E V 2001 *J. Phys. A: Math. Gen.* submitted
[24] Jackson B and Persson M 1995 *J. Chem. Phys.* **103** 6257
[25] Meakin P 1990 *J. Chem. Phys.* **93** 2903
[26] Gates B C 1992 *Catalytic Chemistry* ed B C Gates (New York: Wiley) p 359
[27] Khan K M, Yaldram K, Ahmad N and Qamar-ul-Haque 1999 *Physica* A **268** 89
[28] Engel T and Ertl G 1979 *Adv. Catal.* **28** 1
[29] Williams F G, Aldao C M, Palermo A and Lambert R M 1998 *Surf. Sci.* **412/413** 174