IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Non-thermal transient mobility of O_2 in CO–O_2 surface catalytic reaction: a Monte Carlo simulation study

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys. A: Math. Gen. 37 5125

(http://iopscience.iop.org/0305-4470/37/19/002)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 171.66.16.90
The article was downloaded on 02/06/2010 at 17:58

Please note that terms and conditions apply.

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND GENERAL

J. Phys. A: Math. Gen. **37** (2004) 5125–5133 PII: S0305-4470(04)71840-5

Non-thermal transient mobility of O_2 in CO–O_2 surface catalytic reaction: a Monte Carlo simulation study

K M Khan[1], **P Ahmad**[1] **and M Parvez**[2]

[1] Nuclear Physics Division, Pakistan Institute of Nuclear Science and Technology (PINSTECH), PO Nilore, Islamabad, Pakistan
[2] Computer Division, Pakistan Institute of Nuclear Science and Technology (PINSTECH), PO Nilore, Islamabad, Pakistan

Received 13 November 2003
Published 27 April 2004
Online at stacks.iop.org/JPhysA/37/5125
DOI: 10.1088/0305-4470/37/19/002

Abstract
The catalytic oxidation of CO has already been studied over a square surface through Monte Carlo simulation via a model based on the Langmuir–Hinshelwood (LH) mechanism in which the dissociated adsorption of the O_2 molecule is considered on a pair of vacancies found in the nearest neighbourhood. The results of this study are well known. Here, this reaction system has been studied on the basis of the precursor mechanism, which involves the motion of two oxygen precursors into the first and the third nearest neighbourhood. This study shows that contrary to the dimer–dimer model, the mobility of precursors into the third nearest neighbourhood has no significant effect on the phase diagram of the system. If the reaction of a precursor with chemisorbed oxygen atoms is allowed, the situation changes significantly. In this case, the mobility of precursors has the same effect as observed in the dimer–dimer model. We also have explored the effect of an experimentally observed hot atom adsorption mechanism on the phase diagram of the reaction system. When two oxygen precursors are adsorbed with an average distance of two lattice constants, the second-order phase transition is eliminated. The moment y_{CO} departs from zero, the continuous production of CO_2 starts and the phase diagram closely resembles the experimental one qualitatively.

PACS numbers: 05.10.Ln, 82.70.Dd, 82.65.+r

1. Introduction

Catalytic reactions on solid surfaces involve great complexity and they are thus inherently very difficult to deal with. A comprehensive understanding of such reactions is vital in applied

research. The scientific interest in the study of these processes is due to the emergence of a rich and complex variety of physical-chemistry phenomena, including, e.g., chaotic behaviour, bistability, critical phenomena and irreversible phase transitions, propagation and interference of chemical waves of adsorbed reactants, oscillatory behaviour of some reactions, etc. Oxidation of CO to CO_2 over transition metal catalysts has come to prominence, both for its intrinsic scientific interest and for its immense technological importance [1]. Spurred by such technological interest this reaction has become one of the most widely studied catalytic reactions.

A promising concept of CO–O_2 reaction system was introduced by Ziff, Gulari and Barshad [2] as a computer simulation model and is known as the ZGB model. The interest in the ZGB model arises due to its rich and complex irreversible critical behaviour. In this model the reaction occurs via the Langmuir–Hinshelwood (LH) mechanism, in which both reactants are initially adsorbed on the surface and are in thermal equilibrium with the substrate. The computer simulation details of this model can be found elsewhere [2, 3]. While on the one hand, the ZGB model is of considerable theoretical and conceptual interest for the study and understanding of continuous and discontinuous irreversible phase transitions (IPTs), on the other hand it is a major oversimplification of the actual catalytic process. A controversial feature of the ZGB model concerns the continuous or second-order phase transition (SOPT), which has never been observed experimentally in CO oxidation. Experiments show that the reaction rate begins to increase as soon as CO concentration departs from zero [4–6]. Consequently, different authors have studied variants of the ZGB model in order to give a more realistic treatment to the catalytic oxidation of CO. These improvements include the consideration of the nature of the surface [7], diffusion and desorption of one of the species [8, 9], interaction between neighbours [10], the role of subsurface species [11–14], the effect of the Eley–Rideal mechanism [15, 16], surface reconstruction [17], the effect of the precursor mechanism [18], etc. Despite all these efforts, the reaction system remains inadequately understood.

It has been pointed out that non-thermal processes also play a vital role in the comprehension of catalytic reactions [19–21]. The transient non-thermal mobility caused by the inability of a particle to dissipate the energy instantaneously gained after the formation of a surface bond seems to be a common process in nature. This includes the Eley–Rideal (ER) mechanism (a direct reaction between a gas phase atom and an adsorbed atom) and the precursor mechanism of surface reactions, which involves direct collisions between chemisorbed species and molecules or atoms that are trapped in the neighbourhood of the surface but have not been thermalized. The precursor kinetics is generally different from that characteristic of LH or ER mechanisms [19–21]. Harris and Kasemo [21] have given a detailed discussion on the precursor mechanism. Meakin [15] have studied the dynamics of a 'hot' CO monomer in the ER mechanism using one- and two-dimensional lattices. In two dimensions, the main effect of employing the ER process is the elimination of SOPT and shift of the discontinuous IPT. The moment $y_{CO} \neq 0$, the continuous production of CO_2 starts and steadily increases until $y_{CO} = 0.497$ (± 0.0002) where a first-order IPT terminates the catalytic activity and the surface becomes poisoned by CO.

On the basis of the precursor mechanism, Khan *et al* [22] have recently studied the catalytic production of water through Monte Carlo simulations. This mechanism adds some interesting features in the phase diagram of this catalytic dimer–dimer reaction, which were not seen by considering the LH mechanism [23]. The model shows a steady reactive region, which is limited by the continuous and discontinuous IPTs. The phase diagram is qualitatively similar to the ZGB model; however, the width of the reactive region increases if the mobility

of the precursor is extended to a longer neighbourhood. Some experimentally known facts, such as the occurrence of the first-order transition and the dependence of the reaction rate on the oxygen coverage, are also observed in this model. Khan *et al* [24, 25] have also studied the catalytic formation of ammonia on the basis of a hot hydrogen precursor along the lines envisaged by Harris and Kasemo [21]. The most striking feature of this study is the occurrence of a steady reactive region with continuous production of NH_3, which was not observed in the LH (ZGB-like) model. The results of the model of Khan *et al* are qualitatively similar to those observed in the ZGB model, i.e. the reactive window width and the nature of IPTs is the same. Khan and Albano [26] have also studied the catalytic oxidation of CO on the basis of a non-thermal model, which involves the precursor motion of the CO molecule. This model also yields a steady reactive window, which is separated by the continuous and discontinuous irreversible phase transitions. The width of the window depends upon the mobility of precursors. The continuous transition disappears when the mobility of precursors is extended to the third nearest neighbourhood. The dependence of the production rate on the partial pressure of CO is predicted by simple mathematical equations in the model.

Recent experiments by scanning tunnelling microscopy (STM) on the dissociative adsorption of oxygen molecules on Al (111) and Pt (111) surfaces [27, 28] have pointed to a 'hot atom' mechanism. In this mechanism an oxygen molecule is dissociated into two oxygen atoms, which are propelled apart to distances exceeding 80 Å before equilibrating with the substrate. The hot oxygen atoms react with the adsorbed CO molecule or can stimulate desorption of other co-adsorbed particles [27–29]. The Pt (111) surface can be approximated to a two-dimensional hexagonal lattice where the first nearest-neighbouring (nn) sites have a distance of one atomic spacing. Second and third nn sites have distances of 1.73 and 2 lattice constants, respectively. It was found that the two oxygen atoms appeared in pairs, with average distances of two lattice constants. The appearance of two oxygen atoms in a pair, having one atomic spacing distance, has very small probability [28].

The purpose of this work is to study the effect of the mobility of oxygen atoms (precursors) on the phase diagram of the CO–O_2 reaction system (ZGB model), along the lines envisaged by Harris and Kasemo [21] coupled with the hot adsorption mechanism [28] of O_2. We also intend to see the change in the phase diagram due to the preference of the second nn site over the first nn site since our model is a simplified version of the experimental model [28] in the sense that it considers only those sites of adsorption on which the probability of adsorption of molecules is maximum, namely the second nn sites instead of the usual first nn sites. We have also changed the probability of the reaction between the precursor oxygen and CO from infinite to 0.1 so as to see its effect on the phase diagram. We have chosen a square surface (as used in the ZGB model) for this study. We have ignored the effect of diffusion and desorption of CO in this particular study. The manuscript 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 stated in section 4.

2. Model and simulation

We may write the equations for this reaction system, which incorporates the precursor mechanism, as follows:

$$\mathrm{CO(g)} + \mathrm{S} \rightarrow \mathrm{CO^C} \tag{1}$$
$$\mathrm{O_2(g)} + \mathrm{S} \rightarrow 2\mathrm{O^P} + \mathrm{S} \tag{2}$$
$$\mathrm{O^P} + \mathrm{CO^C} \rightarrow \mathrm{CO_2(g)} + \mathrm{S} \tag{3}$$
$$\mathrm{OP} + \mathrm{S} \rightarrow \mathrm{O^C} \tag{4}$$
$$\mathrm{CO^C} + \mathrm{OC} \rightarrow \mathrm{CO_2(g)} + 2\mathrm{S} \tag{5}$$

where (g) indicates species in the gas phase and S is a vacant surface site. X^P and X^C represent the precursor and the chemisorbed species, respectively.

We consider an infinite reservoir filled with CO and O_2 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 [23, 30]. Periodic boundary conditions are utilized in order to avoid boundary effects. The simulation starts with a clean surface. We shall study the motion of a precursor (and its collision with chemisorbed species) up to the third nearest neighbourhood (two atomic spacings). However, the reaction between two chemisorbed species will be restricted only to the first nearest neighbourhood. 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 are carried out. If all ten runs proceed up to 50 000 MC cycles without the lattice getting 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 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 every 10 MC cycles, so that the final coverage (production rate) is an average taken over 4000 configurations.

The steps involved in the simulation are as follows: a site is randomly picked. If the site is occupied, the trial ends (the molecule is backscattered) else the collision of CO and O_2 molecules is considered with probabilities y_{CO} and $1 - y_{CO}$, respectively. If the colliding molecule is CO then after a collision with this randomly chosen site a CO^C is produced via step (1), which scans its first nearest neighbourhood for the possibility of the reaction step (5). If the colliding molecule is O_2 then the two precursors are produced via equation (2), which move into the 'environment of impact of range R'. We have considered three different ranges of this environment: (i) first nearest neighbourhood ($R = d$), (ii) second nearest neighbourhood ($R = \sqrt{2}d$) and (iii) third nearest neighbourhood ($R = 2d$), where d is the lattice constant. Each environment consists of a specific pattern of the set of sites around the striking site. For example, the first environment consists of four nearest-neighbouring sites. The second environment contains four nearest- and four second-nearest-neighbouring sites whereas the third environment contains all eight sites of the second environment and additional four third-nearest-neighbouring sites. There is a number of possibilities for the reactions of these precursors: all four nn sites of the site of impact are occupied by (i) O^C atoms only, (ii) CO^C molecules only, (iii) a combination of vacancies and O^C atoms, (iv) a combination of vacancies and CO^C molecules, (v) a combination of O^C atoms and CO^C molecules, (vi) a combination of vacancies, O^C atoms and CO^C molecules or (vii) all four nn sites of the site of impact are vacant. In case (i) the trial ends. In case (ii) each precursor picks a CO^C molecule randomly from a particular environment to complete the reaction step (3) and thus the precursors end their life. In case (iii), the adsorption possibility of the two precursors is checked. For this purpose we will explore the effect of first, second and third neighbouring sites. The selection of vacant sites for the adsorption of the two precursors is made in the following ways: (a) one vacant site is selected as the site of impact whereas the second vacant site is picked randomly from the four nn sites, (b) one vacant site is picked randomly from the site of impact and its four nn sites whereas the second vacant site is picked randomly from the four nn sites (one atomic spacing) of the already selected adsorption site, (c) one vacant site is the site of impact whereas the second vacant site is picked randomly from its four second nn sites (1.41 atomic spacing) and (d) one vacant site is the site of impact whereas the second

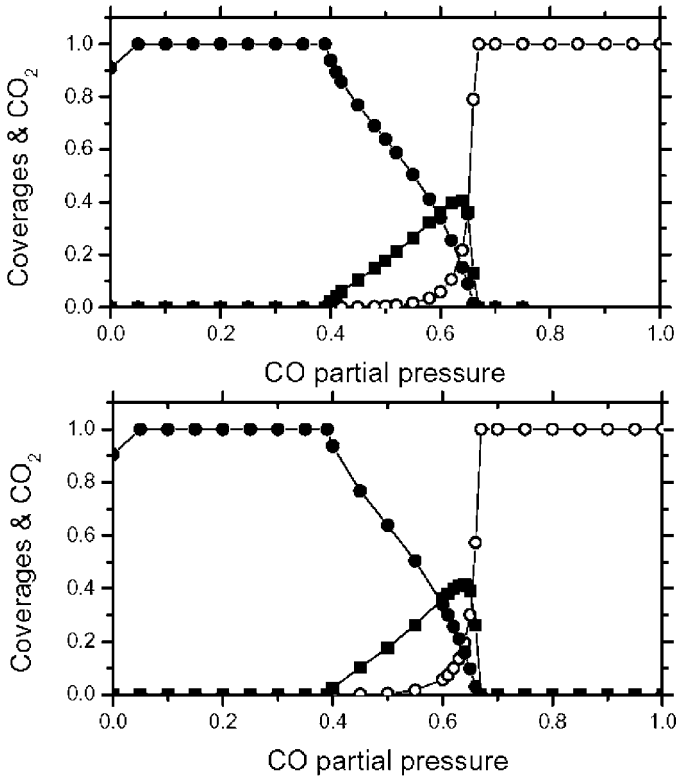

Figure 1. Coverages of O (solid circle), CO (open circle) and the production rate of CO_2 (solid square) plotted as a function of y_{CO} when the adsorption of the two precursors is made such that one vacant site is the site of impact whereas the second vacant site is picked randomly from the four sites of its first nearest neighbourhood and the reaction of a precursor with chemisorbed species is limited to the first nearest neighbourhood (top) and third nearest neighbourhood (bottom).

vacant site is picked randomly from its four third nn sites (two atomic spacings). The trial ends if the second random site is not found to be vacant. In the case that the second site is also vacant then the two precursors are chemisorbed on these two sites. After adsorption, each chemisorbed O^C atom scans its first nearest neighbourhood for the possibility of the reaction step (5). In cases (iv), (v) and (vi) if there is more than one CO^C atom then each precursor picks one CO^C randomly from the four neighbouring sites to complete the reaction step (3) and the trial ends. If there is only one CO^C in the neighbourhood then one precursor picks this CO^C to complete the reaction step (3), whereas the second precursor is chemisorbed on one randomly chosen vacant site via the reaction step (4). After adsorption, the chemisorbed O^C atom scans its first nearest neighbourhood for the possibility of the reaction step (5). In case (vii), the adsorption of the two precursors is made by the same procedure as discussed in case (iii). After adsorption, each chemisorbed O^C atom scans its first nearest neighbourhood for the possibility of the reaction step (5). It is worthwhile to note that this model is physically possible ([26] and references therein).

3. Results and discussion

Figure 1 shows the coverages of the species and production of CO_2 plotted as a function of y_{CO} when the adsorption of the two precursors is made such that one vacant site is the site of

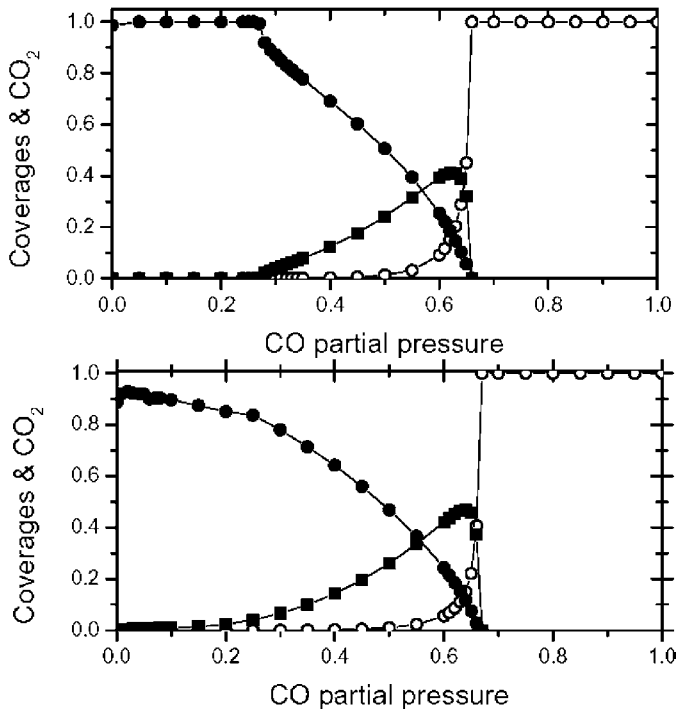

Figure 2. Same as in figure 1 for the case when reaction between the precursor and chemisorbed oxygen atom is considered with probability equal to 0.1.

impact whereas the second vacant site is picked randomly from the four sites of its first nearest neighbourhood and the reaction of a precursor with chemisorbed species is limited to the first nearest neighbourhood (top) and the third nearest neighbourhood (bottom). In the ZGB model a pair of vacancies in the first nearest neighbourhood is required for impingement and the consequent dissociation of the O_2 molecule. The trial ends if a pair of vacancies is not available. On the other hand, in the present model only a single site is required for impingement and the consequent dissociation of the O_2 molecule. This change cannot affect the situation when oxygen partial pressure is high. This is because in this region no CO is available to adsorb on the surface (every CO impinging on the surface is reacted and burnt); only oxygen molecules are available for adsorption on the surface, which get adsorbed on the surface as in the ZGB model. That is why the value of y_1 (where y_1 (y_2) is the partial pressure or feed concentration of the monomer at which the production starts (terminates)) and the qualitative nature of the phase diagram observed in our model is similar to that of the ZGB model. However, the requirement of a single vacancy for accommodating the molecule of O_2 in contrast to the ZGB model plays an important role in the region where CO starts adsorbing on the surface. In the ZGB model, when the supply of oxygen is limited due to the unavailability of a pair of vacancies then CO starts occupying the single vacancies whereas in the present model only a single vacancy is required to accommodate both species (O_2 and CO) on the surface. So, naturally in contrast to the ZGB model the reaction will be sustained to a higher value of feed concentration, which results in the shift of y_2 from 0.525 (in ZGB) to 0.65. It can be seen from the bottom part of figure 1 that the qualitative nature of the phase diagram is not changed when the mobility of the precursor is increased to the third environment. This fact is contrary to

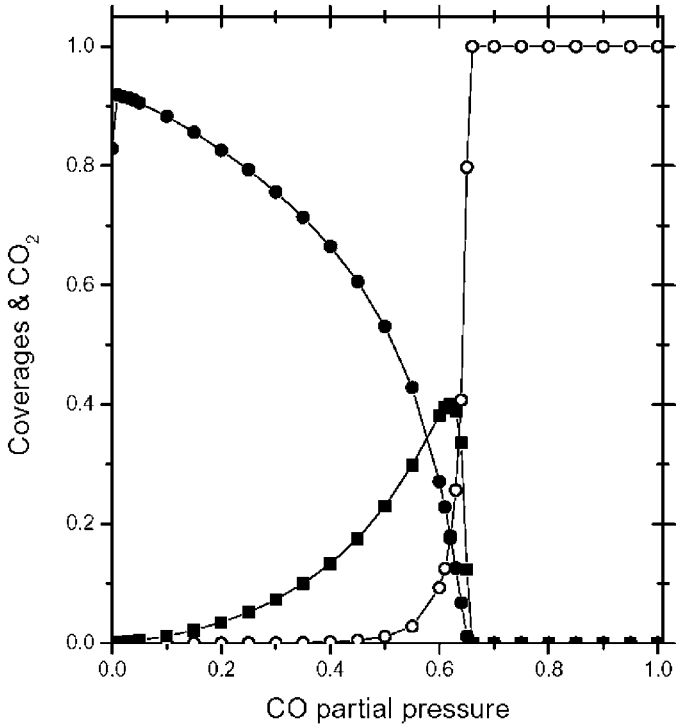

Figure 3. Same as in figure 1 for the case where the adsorption of the two precursors is made such that one vacant site is picked randomly from the site of impact whereas the second vacant sites is picked randomly from the four third nn sites.

the situation as observed in the dimer–dimer ($H_2–O_2$) and monomer–dimer ($CO–O_2$) reaction systems [22, 26]. In both models an increase in the mobility of the precursor (hydrogen or CO) has very significant effect on the phase diagram of the respective system. In these models when the mobility is increased to the third environment, the continuous transition disappears and the moment feed concentration departs from zero continuous production (H_2O or CO_2) starts.

In the above two cases the mobility of the precursor is increased in a region where the opposite reacting species (oxygen) has large islands. Therefore the hopping of precursors in these islands immediately starts production; the moment the feed concentration of the precursor departs from zero. However, in this model the oxygen precursors are hopping in the islands of oxygen itself, which have no direct reaction. Therefore, they cannot affect the phase diagram of the system. However, the introduction of the reaction probability of the precursor with the chemisorbed oxygen atom changes this situation. Figure 2 shows the situation of the phase diagram when the reaction probability of a precursor with a chemisorbed oxygen is fixed to 0.1 and the mobility of the precusor is limited to the first (top) and third (bottom) neighbourhood of the site of impact. It is clear that in this situation the mobility of precursors has the same effect as observed in the dimer–dimer ($H_2–O_2$) and monomer-dimer ($CO–O_2$) reaction systems [22, 26], i.e. the elimination of the second-order phase transition and the start of production the moment the feed concentration departs from zero.

Figure 3 shows the coverages of the species and production of CO_2 plotted as a function of y_{CO} when the mobility of the precursor is limited to the first environment and the adsorption

```
oooo.oooooooooooooooooooooooooooo.oooooooooooooooooooo.ooooooo
oooo.oooooooooooooooooooooooooo.ooooo.oooooooooooooooo.ooooooo
ooooooo.oooooooooo...oooooooooooooooooooo..oooooooooooooooooooo
oooooo.oooooooooooooooooooooooooooooooooooooooooooooooooooooooo
oooooooooooooooooooooooooooooooooooooooooooooooooooooooooooooo
oooooo..oooooooooooooooooooooooooooooooooooooooo.oooooooooooooo
oooo.o..oooooooooooooooooooooooooo.oooooooooooooooooooooooooooo
ooooooooooo.oo.ooooooooooooo.o.ooooooo..oooooooooo.oooooooooooo
ooooooo.ooooooo..oooooooooooo.oooo.oooooooooooooooooooooooooooo
ooooooo.oooooooooo.oooooooooooooooooooooooooo.oooooooooooooooo
oooooooooooooooooooooooooo..oooooooooooooooooooooooooooooooooo
ooooooo.ooo.oo..oooo.o..oooooooooooooooooooooooooooooooo.ooooo
oooooooooo.oooooooooooo..oooooooooooooooo.oooo.oooooooooooo.ooooo
ooooooooo..oo.oooooooooo.oooooooooooooooooooo.oooooooooooooooooo
ooooo....oo.o.oo.oooooooooooooooooooooo..ooo...ooooooooooooooooo
ooooo.oooooooooo..oooooooooooooooooooooooo.oo.o...oooooooooo.ooooo
ooooo.oo.ooo.oo.oooooooooooooooooooooooooooooo.oooooo.oooooooooo
ooo.oo...oooooo.oooooooooooooooooooooooooooooo.ooo.oooooooooooooo
oooo.oooooooooooo.oooooooooooooooooooooo..oooooo.oooo.oooooooooo
.ooo.oooo..oooooooo.oooooooooooooooooooooooooooo.oooooooooooooooo
oooooooooo..oooooooooooooooooooooooooooooooooooo..ooooo..oooooo
o.oooo..ooo.o.oooooooooooooooooooooooooooooooooo..oooo..oooooo
oooooo.ooooo..oooooooooooooooooooo....ooooooo..oo...o.o..ooooooo
oooooooooooooooooooooooooooooooooooooooo.oooo.oo..oooooooooooooo
oooooooooooooooooo.o.oooooooooooooooo.oooooooooo..oooo.o.ooooooo
oooooo.oooooooooo.ooo.oooooooooooooooooooo.oooo...oooo..ooooooooo
ooooo..oooooooooo.oooooooooooooooooooooooo.oooooooooooooooooooo
oooooooooooooooooooooooooooooooooooooooooo...ooooo..o.oooooo..oo
oooooooooooooooooooooooooooooooooooooooooo.ooooooo..oooooooooo.o
```

Figure 4. A snapshot of the coverages when $y_{CO} = 0.14$. Open circles represent oxygen whereas vacancies are represented by dots.

of the two precursors is done in such a way that one vacant site is the site of impact whereas the second vacant site is randomly picked from the four sites of its third nearest neighbourhood. Here, the adsorption of the two hot atoms is relaxed, i.e., the second site of the vacant pair is chosen at a distance of two atomic spacings from the site of impact. Figure 4 shows a snapshot where a large amount of oxygen is seen on the surface. In this situation, if one picks a single vacancy as a site of impact, then there is a small chance that another vacancy at the distance mentioned above can be obtained. Under these conditions, every trial of O_2 impingement will terminate unsuccessfully. However, in the same situation every trial of CO impingement will end in burning of oxygen. As a result, the adsorption rate or the supply of oxygen is reduced at the cost of an increased CO supply and hence the production of CO_2 starts as soon as the value of y_{CO} departs from zero. This situation is very close to the experimental one. The qualitative nature of the phase diagrams shown in figure 3 is the same as shown for the experimental case in [31]. The experimental observation of Wintterlin *et al* [28] that the chance of dissociative adsorption of an O_2 molecule on a pair of nearest neighbouring sites (like the ZGB model) is very small seems to be almost true in our simulation as it does not give a phase diagram (figure 1) comparable to the real one [31]. However, the phase diagrams shown in figure 3 closely resemble the experimental one [31], and it is also consistent with the observation of Wintterlin *et al* [28] that the two hot oxygen atoms appear in pairs, with average distances of two lattice constants.

4. Conclusions

We have studied the catalytic oxidation of CO on a square surface on the basis of the precursor mechanism, which involves the motion of two hot oxygen precursors into the first and third nearest neighbourhoods. It has been observed that contrary to the dimer–dimer model of Khan *et al* [22], the mobility of precursors into the third nearest neighbourhood has no significant

effect on the phase diagram of the system. This is because oxygen precursors are mobile in the islands of oxygen where the reaction of a precursor with the chemisorbed oxygen atoms is not allowed. However, the situation changes significantly if the possibility of such a reaction is considered. In this case, the mobility of precursors has the same effect as observed in the dimer–dimer model of Khan *et al* [22], i.e. the elimination of the second-order phase transition. The moment y_{CO} departs from zero, the continuous production of CO_2 starts, which is a favourable experimental situation. In the aforementioned discussion the adsorption mechanism of the two precursors (which do not have a chance of reaction) was similar to that of the ZGB model, i.e. one is adsorbed on the site of impact whereas the second is adsorbed on a site randomly chosen from the first nearest neighbouring sites. However, the situation changes significantly when the two oxygen precursors are adsorbed with an average distance of two lattice constants (despite the fact that the reaction of a precursor with a chemisorbed oxygen atom is not allowed). In this case the second-order phase transition is eliminated. The moment y_{CO} departs from zero, the continuous production of CO_2 starts. The phase diagram closely resembles the experimental one qualitatively. Last but not least, our objective is to stimulate theorists to formulate a mathematical model, namely the mean field approach, to understand the proposed mechanism, which has proven quite useful for physicists and chemists alike.

References

[1] Engel T and Ertl G 1982 *Chemical Physics of Solid Surfaces and Heterogeneous Catalysis* ed D A King and D P Woodruff (New York: Elsevier) p 4
[2] Ziff R M, Gulari E and Barshad Y 1986 *Phys. Rev. Lett.* **56** 2553
[3] Khan K M, Basit A and Yaldram K 2000 *J. Phys. A: Math. Gen.* **33** L215
[4] Schmatloch V, Jirka I, Heinze S and Kruse N 1995 *Surf. Sci.* **331** 23
[5] Rotermund H H, Lauterbach J and Haas G 1993 *Appl. Phys. A* **57** 507
[6] Ladas S, Imbihl R and Ertl G 1989 *Surf. Sci.* **219** 88
[7] Meakin P and Scalapino D J 1987 *J. Chem. Phys.* **87** 731
[8] Jensen I and Fogedby H C 1990 *Phys. Rev.* A **42** 1969
[9] Evans J W 1993 *J. Chem. Phys.* **98** 2463
[10] Bagnoli F, Sente B, Dumont M and Dagonnier R 1991 *J. Chem. Phys.* **94** 777
[11] Khan K M and Ahmad N 2000 *Physica* A **280** 391
[12] Khan K M and Yaldram K 2000 *Surf. Sci.* **445** 186
[13] Khan K M 2000 *Surf. Sci.* **470** 155
[14] Ahmad N and Khan K.M 2001 *Chem. Phys.* **263** 339
[15] Meakin P 1990 *J. Chem. Phys.* **93** 2903
[16] Khan K M and Ahmed W 2002 *J. Phys. A: Math. Gen.* **35** 2713
[17] Imbihl R and Ertl G 1995 *Chem. Rev.* **95** 697 and references therein
[18] Khan K M and Albano E V 2002 *Chem. Phys.* **276** 129
[19] Wolf N O, Burgess D R and Hoffman D K 1980 *Surf. Sci.* **100** 453
[20] Harris J, Kasemo B and Tornqvist E 1981 *Surf. Sci.* **105** L288
[21] Harris J and Kasemo B 1981 *Surf. Sci.* **105** L281
[22] Khan K M, Albano E V and Monetti R A 2001 *Surf. Sci.* **482** 78
[23] Khan K M, Yaldram K, Ahmad N and Qamar-ul-Haque 1999 *Physica* A **268** 89
[24] Khan K M and Ahmad N 2001 *Chem. Phys. Lett.* **339** 179
[25] Khan K M, Ahmad N and Albano E V 2001 *Surf. Sci.*. **494** 111
[26] Khan K M and Albano E V 2002 *Chem. Phys.* **276** 129
[27] Brune H, Wintterlin J, Trost J, Ertl G, Wiechers J and Behm R J 1993 *J. Chem. Phys.* **99** 2126
[28] Wintterlin J, Schuster R and Ertl G 1996 *Phys. Rev. Lett.* **77** 123
[29] Artsyukhovitch A N and Harrison I 1996 *Surf. Sci.* **350** L199
[30] Khan K M, Yaldram K and Ahmad N 1998 *J. Chem. Phys.* **109** 5054
[31] Albano E V 2000 *Computational Methods in Surface and Colloid Science* ed Borowko (New York: Dekker) p 387