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K M Khan[1], A Basit[1] and E V Albano[2]

[1] Nuclear Physics Division, Pakistan Institute of Nuclear Science and Technology (PINSTECH), PO Nilore, Islamabad, Pakistan
[2] Research Institute of Theoretical and Applied Physical Chemistry (INIFTA), CONICET, UNLP, CIC, Sucursal 4, Casilla de Correo 16, 1900 La Plata, Argentina

Abstract

A simple lattice-gas model for the reaction of CO and NO on an Na-modified surface of a square lattice is studied. The crucial property of the model is Na-induced dissociation of NO, which triggers the catalytic reaction. Some interesting features are added to the phase diagram when the range of Na-induced NO dissociation is studied in the nearest and the next-nearest neighbourhood. The moment CO partial pressure (y_{CO}) departs from zero, the continuous production of CO_2 and N_2 starts. This production remains continuous until a point where the catalytic activity stops and the surface is poisoned with a combination of CO, N and O. The value of poisoning point depends upon the value of Na concentration on the surface.

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1. Introduction

Catalytic reactions on solid surfaces are of great complexity and they are thus inherently very difficult to deal with. Together with the great importance of studies of the catalytic oxidation reaction of CO, 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 0 and 100% for different planes and different temperature range [1, 5]. At a typical operating temperature for a catalytic converter ($\approx$700 K) the adsorption of NO results in the liberation of N_2 gas and in the formation of stable surface oxygen [4, 5]. The vast majority of surface-catalysed reactions proceed via the so-called Langmuir–Hinshelwood (LH) mechanism, in which both reactants are adsorbed and thermally equilibrated with the surface before forming final products. The products eventually desorb into the gas phase.

Ziff, Gulari and Barshad (ZGB) introduced such a gas-lattice model [6] for the heterogeneously catalysed CO–O_2 reaction. Ever since this seminal work, the study of reactive processes using Monte Carlo (MC) simulation has undergone rapid growth [7–16].

Yaldram and Khan applied the ZGB model to the NO–CO surface reaction on square and hexagonal (triangular) lattices [7, 8]. They showed that the type of the lattice and the dissociation rate of NO (r_{NO}) to dissociate it 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. The reactive window is defined as a domain in the parameter space where a steady production of N_2 and CO_2 is observed. Fixing all the parameters except y_{CO}, the partial pressure of CO, the width of the reactive window is defined as $w = y_2 - y_1$, where y_1 is the minimum value of y_{CO} necessary for the reaction to be initiated, and where y_2 is the value of y_{CO} for which the reaction stops due to a poisoning of the surface. A maximum window width W (≈ 0.153) is obtained at $r_{NO} = 1.0$ (i.e. complete dissociation of NO). They have referred to this particular case of $r_{NO} = 1.0$ as the simple LH mechanism for the NO–CO reaction system. 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 (≈ 700 K). This simple mechanism of interest has been used by a number of authors to study different aspects of this reaction system [17–24].

Khan *et al* [24] studied the effect of diffusion of CO, O and N species on the phase diagram of the system for the same lattice. This consideration leads to a reactivity of the system only in the case of N diffusion. The reactive window bounded by continuous and discontinuous transition is also dependent on the probability of diffusion. For maximum diffusion probability, the continuous transition occurs at $y_{CO} \approx 0.203$ while the discontinuous transition occurs at $y_{CO} \approx 0.297$. Recently, Dickman *et al* [23] have shown theoretically that surface diffusion of nitrogen can only lead to an active state on a square lattice for this reaction system. Khan [14] has also studied the influence of subsurface oxygen in NO–CO reaction on the (001) surface and subsurface of a simple cubic structure through MC simulation. The model is based on the LH mechanism. The introduction of a single subsurface site in the usual four nearest-neighbouring sites of the square lattice generates a steady reactive state (SRS), the region of continuous production, in this reaction system.

The study of adsorption and co-adsorption with a small number of alkali atoms on metal surfaces is a topic of current research. It is well known that the addition of small amounts of alkali on transition metal surfaces strongly modifies the selectivity and reactivity of some heterogeneously catalysed reactions [25–33]. From both theoretical and experimental studies, it has been concluded that this 'promotion effect' is primarily of short range. Nevertheless, at the working temperature of some real catalysts ($\approx T = 700$ K) the alkali adlayer is no longer stable and the promotion effect is lost due to desorption of the alkali atoms. On the other hand, co-adsorbed oxygen thermally stabilizes the alkali adlayer [26, 34]. This fact is essential to achieve a long-time promotion effect. When the Pt(111) surface is modified with sodium, the alkali induces NO dissociation due to weakening of the N–O bond [35]. Palermo *et al* [36] have studied this reaction system over the Pt surface under conditions of promotion (EP) by Na. They found that the EP effect depends critically on Na-induced dissociation of chemisorbed NO. A more detailed understanding of the promotion by Na of the catalytic reduction of NO is therefore of great interest.

Very recently, Williams *et al* [37] have performed MC simulation of the NO–CO reaction on Na-promoted platinum. They approximated the Pt surface by a simple triangular (hexagonal) two-dimensional lattice of sites. In this model the Na-induced NO dissociation is

the key factor. First, NO is adsorbed on a single site in the neighbourhood of the site occupied by Na. Then it may dissociate into N and O atoms if another vacant site is available in the next-nearest neighbourhood of NO. The adsorbed Na sites block the adsorption of CO molecules on these sites. Through this model, they have not studied the irreversible phase transition as a function of system parameters. They were principally interested in the influence of the alkali coverage on the kinetic behaviour of the system with respect to the rates of CO_2, N_2 and N_2O formation and the resulting nitrogen selectivity. In their model they allowed both NO and CO to desorb at a finite rate. Also they allowed two (or more) Na atoms to sit next to each other in the neighbourhood (figure 5 of [3]), which seems to be unlikely. This is because upon adsorption Na transfers some electronic charge to the surface, so it becomes highly polarized, and due to this strong dipole repulsion Na atoms are far away from each other on the surface. However, their model satisfactorily accounts for the principal features of experimental data involving EP of Na on the NO–CO reaction on Pt surface.
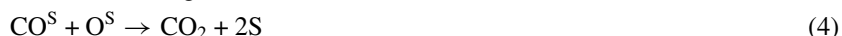
Here, we shall also simulate the reaction system of CO and NO on the Na-modified surface through MC simulation. However, our model has a number of differences from the model of Williams *et al* [37], such as the following.

(i) Our main interest is to explore the effect of Na concentration on the irreversible phase transitions, coverages of the species and the window width of the steady reactive region (if any).
(ii) The reaction system is studied on a square surface.
(iii) The Na atoms are distributed randomly over a square lattice in such a way that adsorption of Na atoms next to each other is not allowed.
(iv) Desorption of both NO and CO are completely ignored.
(v) The simple LH model of Yaldram and Khan [8], in which NO always adsorbs on two vacant nearest-neighbouring sites, is considered to study this reaction system.

The paper is structured as follows: in the next section the reaction model and the simulation procedure is discussed. The results are presented and discussed in section 3. Finally the conclusions are inferred in section 4.

2. Model and simulation

The model can be written in the form of the following equations.

$$CO(g) + S \rightarrow CO^S \tag{1}$$
$$NO(g) + 2S(Na) \rightarrow N^S + O^S \tag{2}$$
$$N^S + N^S \rightarrow N_2(g) + 2S \tag{3}$$
$$CO^S + O^S \rightarrow CO_2 + 2S \tag{4}$$
$$CO(g) + S(Na) \rightarrow \text{no reaction} \tag{5}$$
$$NO(g) + 2S \rightarrow \text{no reaction} \tag{6}$$

where S is an empty surface site, (g) refers to the gas phase, S(Na) is the Na-activated site and X^S represents the X adatom.

The reaction step (1) depicts the adsorption of CO. The chemisorption of CO on the clean (100) surface of palladium comes about by a ligand association reaction, and the resulting structure can be ascertained by low-energy electron diffraction (LEED) [40]. Generally, CO molecules are adsorbed in molecular form on transition metal surfaces with the sticking coefficient close to unity [2, 41]. The adsorption of NO on Pt(100) has been studied by thermal desorption spectroscopy (TDS) [42, 43], LEED [44], vibrational spectroscopy [45]

and photoelectron spectroscopy [46]. All experiments conclude that NO adsorbs molecularly at room temperature and dissociates upon heating above ~380 K [2]; however, when the Pt surface is modified with sodium, the alkali metal dissociates NO due to weakening of the N–O bond [35] as already mentioned in the introduction (reaction step (2)). As mentioned earlier, the adsorption of NO at ~700 K results in the liberation of N_2 gas (reaction step (3)) and in the formation of a stable surface oxygen species. These surface oxygen species are then utilized by CO molecules to be oxidized into CO_2 [4,5]. After formation on the surface, CO_2 is rapidly desorbed [40] as shown by reaction step 4.

The key feature of this model is the Na-induced dissociation step (2), for which we assume that NO molecule dissociates only when an NO molecule impinges on an Na-activated site that is nearest neighbour or next-nearest neighbour to a site occupied by Na. This short-range effect of Na on co-adsorbed NO is fully consistent with the definitive theoretical study by Lang *et al* [38]. They showed that the effect of alkali promoters on adjacent adsorbates is local in nature.

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, 39]. Periodic boundary conditions are used in order to avoid boundary effects. The equilibrium coverages (average number of species per lattice site) 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 becoming poisoned, the particular point is considered to be within the 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 the final coverage (production rate) is an average taken over 4000 configurations. The production rate is the average production of CO_2 and N_2 per MC cycle, per lattice site.

Based on the simulation procedure we divide our model into two parts. The first part belongs to the first Na-activated zone, which consists of Na-occupied sites and their nearest-neighbouring (nn) sites. The second part of the simulation belongs to the Na-activated zone which consists of Na-occupied sites and their nearest- and next-nearest-neighbouring (nnn) sites. The steps involved in the simulation are as follows.

(a) A certain number of Na atoms are randomly distributed over the initially empty lattice. Na atoms cannot sit next to each other on the surface. The effects of different Na coverages are examined.

(b) A site is picked at random. If the site is occupied the trail ends. If the selected site is vacant then a CO or NO molecule is selected randomly for adsorption with relative probabilities y_{CO} and $1 - y_{CO}$ respectively.

(c) If CO happens to be adsorbed then another check is made that the vacant site does not belong to a particular Na-activated zone. If the randomly chosen vacant site belongs to a particular Na-activated zone then the trail ends, else CO is adsorbed on it. The nn sites of the adsorbed CO molecule are scanned for the presence of an O atom in order to complete reaction step (4).

(d) If NO happens to be adsorbed then one of the following events occurs:

   (i) the selected site is not in a particular Na-activated zone, in which case the trial ends and a new molecule is selected;
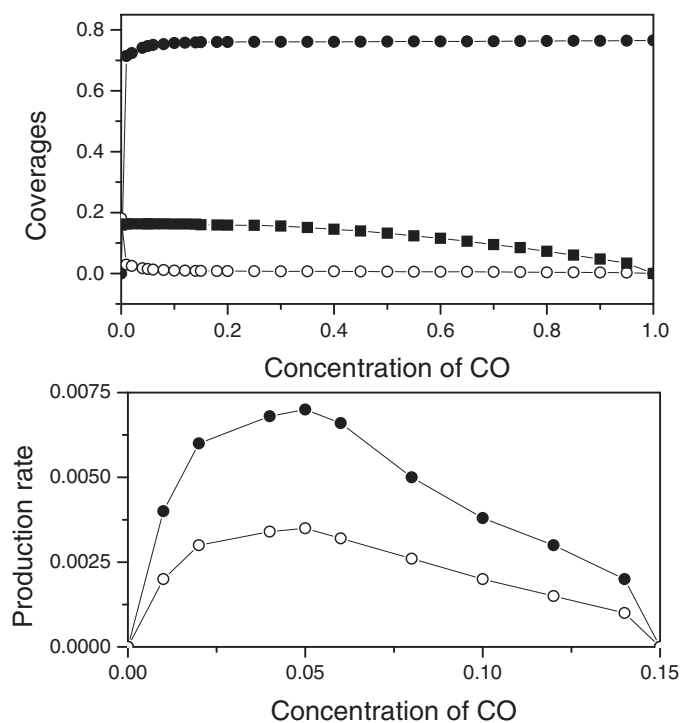
Figure 1. The coverages (top) of CO (solid circle), O (open circle) and N (solid square) versus concentration of CO and production rates (bottom) of CO_2 (solid circle) and N_2 (open circle) versus concentration of CO for the case when first Na-activated zone is taken into account and Na is 5% on the surface.

(ii) the selected site is in a particular Na-activated zone, in which case its nn sites are also scanned randomly for the presence of another vacancy.

The molecule dissociates into N^S and O^S atoms if a second vacancy is found otherwise the trial ends. The nn sites of N^S and O^S atoms are then examined for the presence of N^S and CO^S in order to complete reaction steps (3) and (4), respectively.

3. Results and discussion

Figure 1 shows the phase diagram of the reaction system in the first Na-activated zone when Na concentration is 0.05. For $y_{CO} = 0$, the coverages of O (θ_O), N (θ_N) and vacancies (θ_V) $\approx 0.18, 0.16$ and 0.61 respectively. The moment $y_{CO} > 0 (y_{CO} = 0.01)$, the production of both CO_2 and N_2 starts and the coverage of CO (θ_{CO}) shoots to ≈ 0.71, whereas θ_O attains a value of ≈ 0.03. However, the θ_N remains the same. It is important to mention that here $y_1 = 0$ and hence the reactive window width reduces to y_2. With further increase in y_{CO}, θ_{CO} shows a slow increase whereas θ_O shows a slow decrease with continuous productive activity. However, this productive activity stops at $y_2 = y_{CO} = 0.155 \pm 0.005$ and the surface is poisoned with a combination of CO, O and N. In this combination, the value of θ_{CO} is almost constant for the whole range of y_{CO}. Figure 2 shows a phase diagram of the first Na-activated zone for the case of 0.15 Na concentration. It can be seen that the situation of coverages has now been
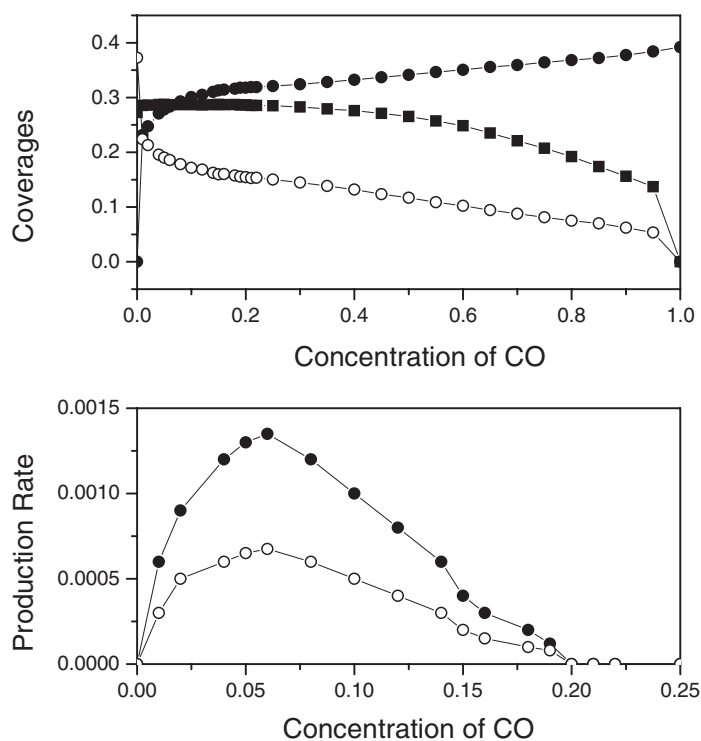
Figure 2. The same as in figure 1 for 15% Na concentration.

changed. This is because 5% Na activates a smaller area whereas 15% Na activates a larger area for the adsorption of NO. For $y_{CO} = 0$, the values of θ_O, θ_N and θ_V are ≈ 0.37, 0.27 and 0.21 respectively. The moment $y_{CO} \neq 0$ ($y_{CO} = 0.01$), the productive activity starts and θ_{CO} shoots to ≈ 0.23 whereas θ_O and θ_N attain values ≈ 0.22 and 0.29 respectively. This productive activity stops at $y_2 = y_{CO} = 0.200 \pm 0.005$ and the surface is poisoned with a combination of CO, O and N. However, in this combination the trend of the coverages is different from that of figure 1. The value of θ_{CO} continuously increases whereas the values of θ_O and θ_N continuously decrease with increase in y_{CO}. It is also observed that the position of maximum CO_2 and N_2 production rates is observed at the same value of y_{CO} and also promotion and poisoning of the N_2 rate resembles that of the CO_2 rate. This is because both production rates depend on the dissociation of NO molecule.

It is well known that the poisoning of a square lattice takes place by a process of 'chequerboarding' of N atoms [19, 20]. In the model of Khan *et al* [24] N diffusion halts the poisoning of the square lattice, because it breaks up the chequerboarded states. Also it is not too surprising that such poisoning is halted on a hexagonal (triangular) surface [7], where chequerboarding of N atoms cannot occur geometrically. In the model of Khan [14], the chequerboarding of N atoms is also broken up easily by the introduction of a single subsurface site (in addition to four surface sites). This single subsurface site (nearest neighbour of the other four surface sites) provides the ability of an NO molecule to adsorb (in dissociated form) on a single surface site. Here, in the present model, the blocking of CO adsorption in the Na-activated region also breaks the chequerboarding process of N atoms.
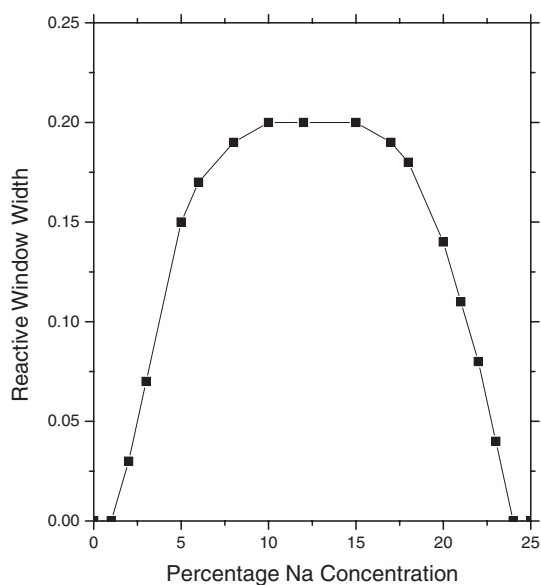
Figure 3. The reactive window width (W) versus percentage Na concentration.

Figure 3 shows window width (W) plotted against percentage Na concentration. The value of W increases with increase in Na concentration (region 1), attains a maximum value for a wide range of Na concentration (region 2) and then decreases with further increase in Na concentration (region 3). For small Na coverage the surface consists mainly of isolated active zones separated by extensive inactive regions in which no reaction takes place. Since N and O are produced only near an Na-occupied site, reaction may occur in the active zones and at their boundaries. Let us concentrate on region 1 for Na concentration equal to 0.03. This gives a small active area for NO adsorption and a large inactive area for CO adsorption. With further increase in Na concentration (say $\approx$0.05), the active area for NO adsorption is increasing whereas the inactive area for CO adsorption is decreasing. Therefore, the catalytic activity will be sustained for larger value of y_{CO} (as compared with the case of 0.03) due to availability of larger clusters of Na-activated zones. Then in region 2, both the active area for NO adsorption and inactive area for CO adsorption have an optimum level and the catalytic activity is sustained for the same value of y_{CO}. However, in region 3 the active area for NO adsorption becomes larger than the inactive area for CO adsorption. For small values of y_{CO}, the increased clusters of Na-activated zones burn the small amount of CO quickly and hence window width decreases. Figure 4 shows the position of the coverages on the surface for Na concentration equal to 0.21 where for small values of y_{CO} the coverage of O is greater than the coverage of CO. The catalytic activity completely stops when Na concentration is >0.24.

Figure 5 shows a plot of window width (W) versus percentage Na concentration for the second Na-activated zone. It can be seen that the qualitative nature is the same as observed in figure 3. However, for a particular value of Na concentration the value of W in the present case is larger than that in the case of figure 3. For the particular case of Na concentration equal to 0.05, the value of W in the first Na-activated zone is 0.15 whereas this value shoots to 0.81 in the second Na-activated zone. As mentioned earlier the reactions occur in the active zones and at their boundaries. 5% sodium activates a smaller area (four sites per Na site) in the first
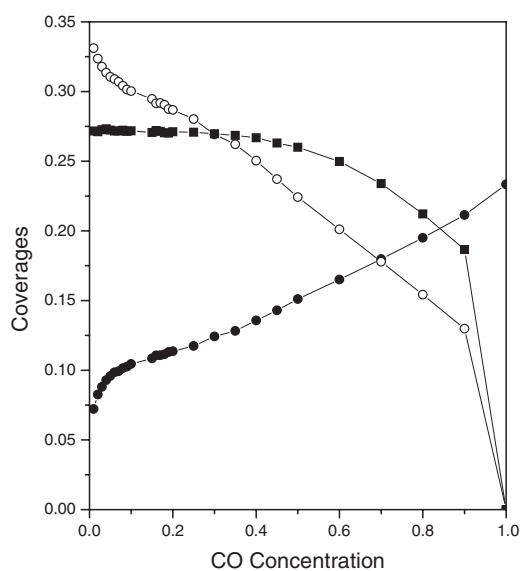
Figure 4. Coverages of the reacting species as shown in figure 1 (top) for 21% Na concentration.
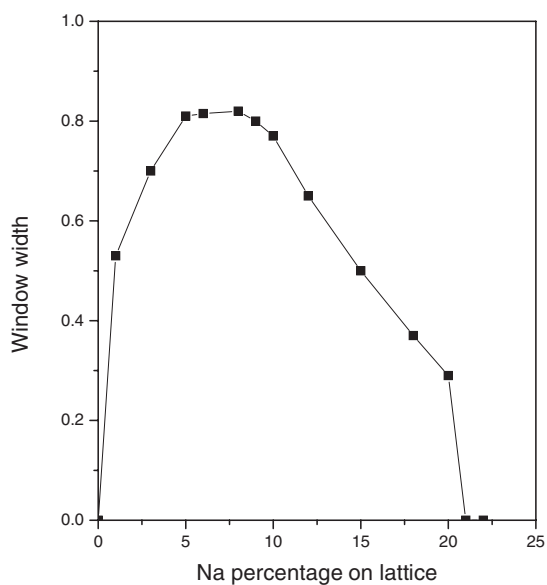

Figure 5. Same as in figure 3 for second Na-activated zone.

Na-activated zone whereas in the second Na-activated zone a larger area (eight sites per Na site) is activated for the reactions to occur. Therefore, a larger reactive window is obtained in the second zone. Also the catalytic activity stops earlier in this particular zone. Here, the catalytic activity completely stops when Na concentration is >0.21. We have also explored the effect of Na concentration distributed randomly in such a way that two or more Na atoms can sit next to each other (as studied by Williams *et al* [37]). It was observed that for 5% Na concentration, no reactive window is observed in the first activated zone. However, for the
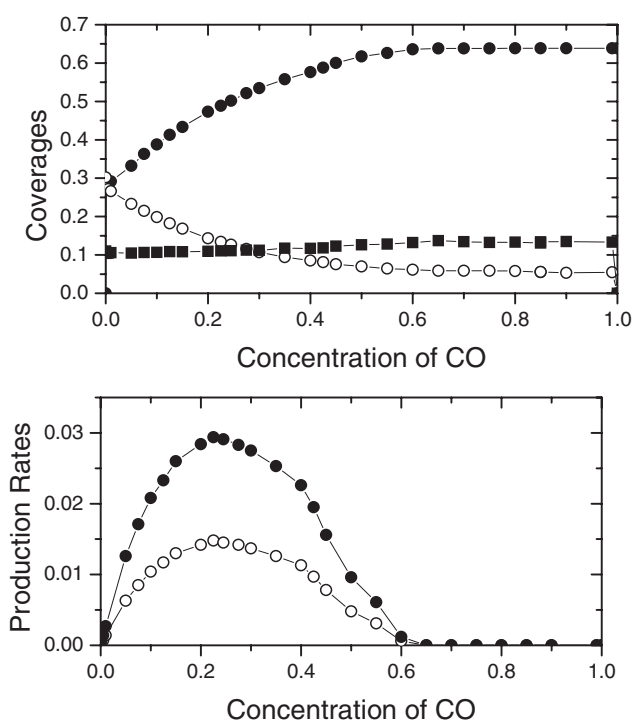
Figure 6. The same as in figure 1 for the case of the second Na-activated zone when Na are allowed to be adsorbed next to each other on the surface.

second activated zone a window width is observed which has a smaller value (≈ 0.60) than that observed in the present case. This situation is shown in figure 6.

4. Conclusions

A simple ZGB-like lattice-gas model for the reaction of CO and NO on an Na-modified square surface has been studied. The Na-induced NO dissociation in the model breaks the usual chequerboarding process of N atoms on the square surface. In this theoretical model we have explored the effect of the amount of Na (randomly distributed on the surface) on the phase diagram of the system. Some interesting features of the reaction system are observed. 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 a particular point, where the catalytic activity stops and the surface is poisoned with a combination of CO, N and O. The position of this transition point (and hence the width of the reactive window) depends upon the concentration of Na on the surface. Remarkably, for a particular value of Na concentration, the reactive window width increases rapidly when the range of Na-induced NO dissociation is extended from the first-nearest neighbourhood to the second-nearest neighbourhood.

Acknowledgment

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] Khan M A, Yaldram K, Khalil G K and Khan K M 1994 *Phys. Rev.* E **50** 2156
[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] Khan K M, Basit A and Yaldram K 2000 *Surf. Sci.* **469** 65
[14] Khan K M 2000 *Surf. Sci.* **470** 155
[15] Khan K M and Ahmad N 2001 *Chem. Phys. Lett.* **339** 179
[16] Khan K M, Albano E V and Monetti R A 2001 *Surf. Sci.* **481** 78
[17] Brosilow B J and Ziff R M 1992 *J. Catal.* **136** 275
[18] Cortes J, Puschmann H and Valencia E 1998 *J. Chem. Phys.* **109** 6086
[19] Cortes J and Valencia E 1998 *Chem. Phys.* **229** 265
[20] Meng B, Wienberg W H and Evans J W 1993 *Phys. Rev.* E **48** 3577
[21] Cortes J, Puschmann H and Valencia E 1996 *J. Chem. Phys.* **105** 6026
[22] Yaldram K, Khan K M, Ahmad N and Khan M A 1993 *J. Phys. A: Math. Gen.* **26** L805
[23] Dickman A G, Grandi B C S, Figueiredo W and Dickman R 1999 *Phys. Rev.* E **59** 6361
[24] Khan M A, Yaldram K, Khalil G K and Khan K M 1994 *Phys. Rev.* E **50** 2156
[25] Mross W D 1983 *Catal. Rev. Sci. Eng.* **25** 591
[26] Paal Z, Ertl G and Lee S B 1981 *Appl. Surf. Sci.* **8** 231
[27] Ertl G, Lee S B and Weiss M 1982 *Surf. Sci.* **114** 527
[28] Norskov J K, Holloway S and Lang N D 1984 *Surf. Sci.* **137** 65
[29] Markert K and Wandelt K 1985 *Surf. Sci.* **159** 24
[30] Pirug G and Bonzel H P 1988 *Surf. Sci.* **199** 371
[31] Albano E V 1982–3 *Appl. Surf. Sci.* **14** 183
[32] Albano E V 1984 *Surf. Sci.* **141** 191
[33] Albano E V 1989 *Surf. Sci.* **215** 333
[34] Heskett D 1988 *Surf. Sci.* **199** 67
[35] Harkness L R and Lambert R M 1997 *J. Chem. Soc. Faraday Trans.* **101** 3759
[36] Palermo A, Lamkert R M, Harkness I R, Yentekakis I V, Marina O and Vayenas C G 1996 *J. Catal.* **161** 471
[37] Williams F G, Aldao C M, Palermo A and Lambert R M 1998 *Surf. Sci.* **412/413** 174
[38] Lang N D, Halloway S and Norskov J 1985 *Surf. Sci.* **150** 24
[39] Khan K M, Yaldram K, Ahmad N and Qamar-ul-Haque 1999 *Physica* A **268** 89
[40] Behm R J, Christmann K, Ertl G and Van Hove M A 1980 *J. Chem. Phys.* **73** 2984
[41] Ertl G, Lee S B and Weiss M 1982 *Surf. Sci.* **114** 515
[42] Gorte R J, Schmidt L D and Gland J L 1981 *Surf. Sci.* **109** 367
[43] Gohndrone J M and Masel R I 1989 *Surf. Sci.* **209** 44
[44] Bonzel H P, Brodén G and Pirug G 1978 *J. Catal.* **53** 96
[45] Gardner P, Tüshaus M, Martin R and Bradshaw A M 1990 *Surf. Sci.* **240** 112
[46] Bonzel H P and Pirug G 1977 *Surf. Sci.* **62** 45