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Catalytic reduction of NO with H₂ on a square surface: a Monte Carlo simulation study

K M Khan and A Khan

Nuclear Physics Division, Pakistan Institute of Nuclear Science and Technology (PINSTECH),
PO Nilore, Islamabad, Pakistan

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Abstract

The catalytic reduction of NO with H₂ is of considerable interest due to the pollution effects of NO in air. Previously, computer simulation studies of this reaction system have been made on the basis of a Langmuir–Hinshelwood (thermal) mechanism. We have studied a model through Monte Carlo simulation, which assumes that the reaction can proceed via a non-thermal (precursor) mechanism. When the motion of the precursor is taken into the first nearest neighbourhoods and NO is always adsorbed in a dissociated form, the model predicts a very small steady reactive window, which is limited by two irreversible phase transitions. However, diffusion of N atoms widens the reactive window considerably. When NO is adsorbed as a molecule (leading to dissociated adsorption if a vacancy pair is available), the motion of the precursor in the first neighbourhood does not provide any reactive region. Remarkably, diffusion of N atoms cannot change the situation in this case. However, desorption of NO provides some interesting results.

1. Introduction

Together with the great importance of studies of the catalytic oxidation reaction of CO and the reduction of NO by CO, there has also been great interest in the reduction of NO with H₂. These reactions are important in automotive exhaust emission control. The kinetics of such heterogeneously catalyzed reactions often exhibits a rich and complex nonlinear dynamic behaviour. Ever since the introduction of the Ziff, Gulari and Barshad (ZGB) [1] gas-lattice model for the heterogeneously catalyzed CO–O₂ reaction, the study of reactive processes using Monte Carlo (MC) simulation has undergone rapid growth [2–8]. Yaldram and Khan [2, 9] 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}) to dissociate 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 N₂ and CO₂ is observed for a hexagonal lattice when $r_{\text{NO}} > 0.80$. For $r_{\text{NO}} < 0.8$, no reactive window is obtained even for a hexagonal lattice. A maximum window width

(≈ 0.153) is obtained at $r_{\text{NO}} = 1.0$ (i.e. complete dissociation of NO). They have referred to this particular case of $r_{\text{NO}} = 1.0$ as the simple Langmuir–Hinshelwood (LH) mechanism for the NO–CO reaction system. This simple mechanism of interest has been used by a number of authors to study different aspects of this reaction system [9–18].

The catalytic reduction of NO with H₂ is one of the important processes that occur on the surface of a catalyst used in automobile exhausts. Yaldram and Khan [4] have proposed and studied various lattice gas models of this reaction system through MC simulation on square and hexagonal lattices. All proposed models are based on the LH (thermal) mechanism and assume dissociated adsorption of a NO molecule. They have not studied the molecularly adsorption of NO at all. In their study, Yaldram and Khan [4] have highlighted 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 steady reactive state (SRS). For the case of a square lattice, they studied four different models. In model M1 both diffusion and desorption of the reactants was ignored. In model M2, the diffusion of only H atoms was considered. The diffusion of H atoms as well as their recombination and desorption was taken into account in model M3. Model M4 considers diffusion of N atoms. All the above-mentioned first three models (M1, M2 and M3) gave a final poisoned state for all feed concentrations. For model M1 there was a continuous crossover from one poisoned state to another, while for the M2 and M3 models an irreversible phase transition separated one poisoned state from the other. However, the diffusion of N atoms in model M4 was found to be crucial to the evolution of the system towards a final SRS. Even the slightest movements of the N atoms produced an irreversible phase transition at $y_1 = y_{\text{H}} \approx 0.54$ (where y_{H} is the feed concentration of H₂ gas), which separated a poisoned state from a SRS. On the other hand, for the hexagonal lattice the M3 model led the system towards a SRS. An irreversible phase transition was obtained at $y_1 = y_{\text{H}} \approx 0.54$ (where y_{H} is the feed concentration of H₂ gas), which separated a poisoned state from a SRS. The role of increasing the number of nearest neighbouring sites is seen to be similar to that of the diffusion of N atoms.

The transient non-thermal mobility caused by the inability to dissipate the energy instantaneously gained by a particle after formation of the surface bond seems to be a common process in nature. Brune *et al* [19] have demonstrated (by means of scanning tunnelling microscopy observations) that oxygen molecules striking the Al(111) surface not only dissociate upon adsorption but also dissipate part of their excess energy in degrees of freedom parallel to the surface. By taking into account this experimental fact, Pereyra and Albano [20] have studied the influence of the ‘hot’ dimer adsorption mechanism on the kinetics of a monomer–dimer (CO–O₂) catalytic reaction. ‘Hot’ dimers are molecules which, after adsorption, dissociate and each of the remaining ‘hot’ atoms flies apart up to a maximum distance R from the original adsorption site. The catalytic reaction of H₂ and O₂ on polycrystalline Pt has been studied with quartz crystal microbeam data in the early work of Harris *et al* [21]. They have analysed the data by means of a mean field approach and have shown that this particular reaction system is an example of a precursor mechanism. Harris and Kasemo [22] have given a detailed discussion on a precursor mechanism of surface reactions. This mechanism involves direct collisions between chemisorbed species and molecules or atoms that are trapped in the neighbourhood of the surface but have not thermalized. The precursor kinetics is generally different from those characteristics of the LH or ER mechanisms [21–23]. On the basis of the precursor mechanism, Khan *et al* [24] have recently studied the catalytic production of water through MC simulations. Through this model, they have reproduced some experimental results of the real system. Khan *et al* [25, 26] have also studied the catalytic formation of ammonia based on a hot hydrogen precursor along the lines envisaged by Harris and Kasemo [22]. The most interesting feature

of their model is that it yields a steady reactive window, which is separated by continuous and discontinuous irreversible phase transitions. The phase diagram is qualitatively similar to the well-known ZGB model. 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 objective of this paper is to study a non-thermal surface model along the lines envisaged by Harris and Kasemo [22] for the catalytic reduction of NO with H₂ through MC simulation. The diffusion and desorption of the reactants will also be considered in this work. Here, we will consider dissociated adsorption of NO molecules as well as its molecular adsorption. The paper is structured as follows: in the next section the reaction mechanism and the simulation procedure is discussed. The results are presented and discussed in section 3. Finally, the conclusions are inferred in section 4.

2. Models and simulation procedure

Based on dissociated and molecular adsorption of NO, we may divide the model into two parts.

2.1. Model A

In model A, NO is adsorbed into its dissociated form. We may write the equations for this model, which incorporates the precursor mechanism, as follows:



Here (g) indicates the species in the gas phase and S is a vacant surface site. The precursor and chemisorbed adatoms are represented by X^P and X^C, respectively.

We consider an infinite reservoir filled with hydrogen and NO dimers with partial pressures y_{H} and $1 - y_{\text{H}}$, respectively. This reservoir is in contact with a surface which is simulated by means of a square lattice of linear dimension $L = 256$. 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 [7, 27]. Periodic boundary conditions are used in order to avoid boundary effects. The simulation starts with a clean surface. If the striking molecule is H₂ then it requires only one site to be vacant in order to produce two precursors (equation (3)). If the striking molecule is NO then it requires two sites to be vacant in order to produce two chemisorbed atoms (equation (1)). We will study the motion of a precursor (and its collision with chemisorbed species) up to the first nearest neighbourhood. Therefore, in our simulation there is only one variable y_{H} . The equilibrium coverages are measured as a function of y_{H} . In order to locate the critical points ten independent runs, each up to 50 000 MC cycles, were 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 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 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) A site is picked randomly. If the site is occupied the trial ends (the molecule is backscattered), else collision of the molecules H_2 and NO is considered with probability y_H and $1 - y_H$, respectively.
- (b) If the colliding molecule is NO then its four neighbouring sites are also scanned for the presence of a vacancy. The trial ends if no vacancy is found in the neighbourhood. For the case that a second vacant site is available then step (1) takes place to produce two chemisorbed atoms N^C and O^C .
- (c) If the colliding molecule is H_2 then, after collision with this randomly chosen site, two precursor atoms H^P are produced via step (3), which move into the 'environment' of impact of R . This environment consists of four nearest-neighbouring sites.
- (d) If, during its motion in the environment, a precursor H^P strikes a chemisorbed atom O^C then reaction step (4) takes place and the precursor ends its life. In a similar way if a precursor H^P strikes with a chemisorbed radical OH^C then reaction step (5) takes place and the precursor ends its life. A water molecule is formed which desorbs from the surface and the site occupied by OH^C is vacated. The collision of this precursor atom is taken at random so that the collision of H^P with OH^C or O^C is equally probable. In the case that the precursor does not find any chemisorbed reacting species within a particular environment then it takes one vacant site (randomly chosen) from the environment to be chemisorbed (step (6)) and the precursor atom ends its life. This chemisorbed atom scans its four neighbouring sites for the presence of O^C or OH^C in order to complete reaction steps (7) and (8), respectively. If O^C is found then OH^C is formed and the site occupied by H^C is vacated. If OH^C is found then H_2O is formed, which desorbs and the sites occupied by H^C and OH^C are vacated. It should be noted that after adsorption the O^C atoms also scan their respective nearest neighbourhoods in order to complete possible reaction step (7).
- (e) If both precursors of the H_2 molecule do not end their life through any of the above-mentioned ways, then they return to the gas phase via step (9) and hence the trial ends. If one of the two precursors does not end its life through any of the above-mentioned ways, then it is adsorbed on the surface through reaction step (6).

In order to introduce diffusion of a particular species, simulation step (a) is modified. If the randomly selected site is occupied by a species other than that particular one the trial ends. If the randomly site is occupied by a species of interest, its four nearest-neighbouring sites are scanned for a vacancy. If a vacancy is found the species is moved onto this vacant site and the previous site is vacated. After diffusion, its nearest neighbourhood is scanned for a possible reaction step.

2.2. Model B

In model B, NO is adsorbed onto a single vacant site as a molecule. It dissociates if a vacant site is available in its first nearest neighbourhood. For this model, equation (1) of model A is replaced by the following three equations:



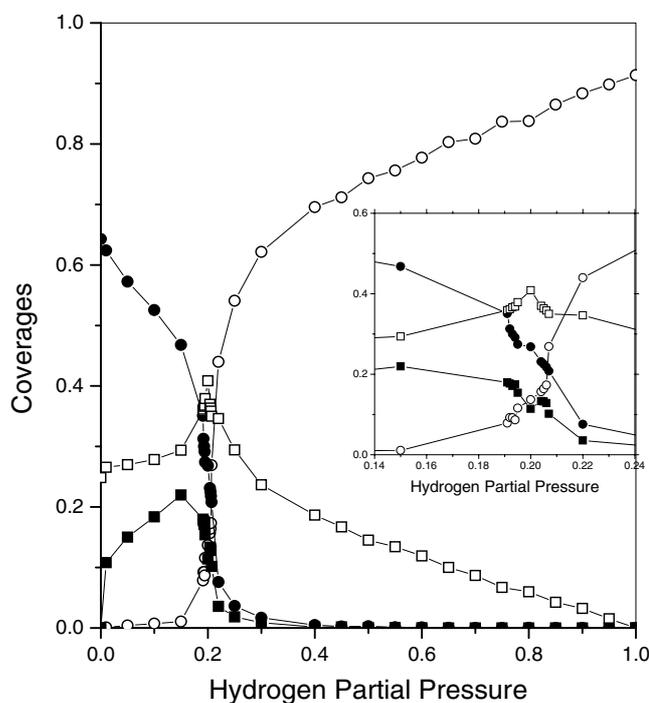


Figure 1. Coverages of O (full circle), H (open circle), N (open square) and OH (full square) plotted as a function of hydrogen partial pressure. The inset shows a magnified portion of the SRS.

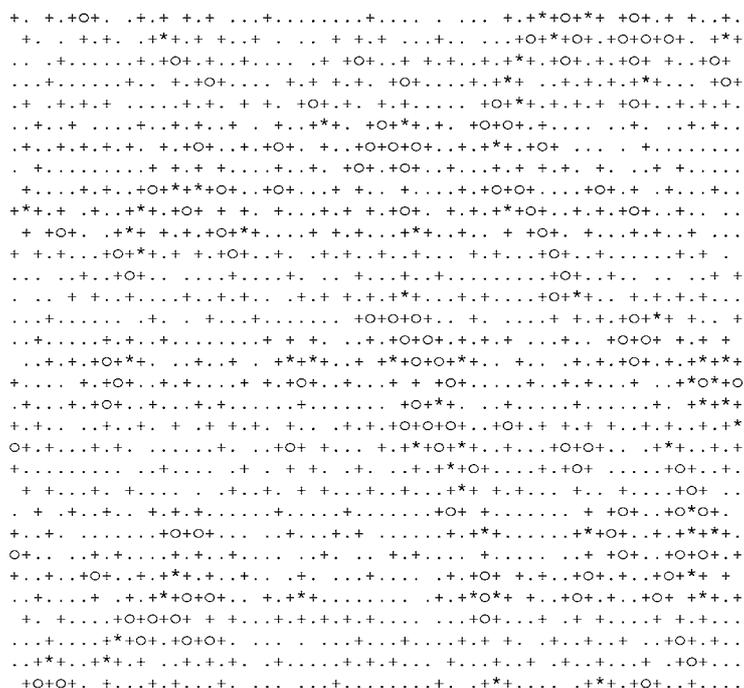


In order to incorporate the three equations, the simulation step (b) of model A is modified as follows:

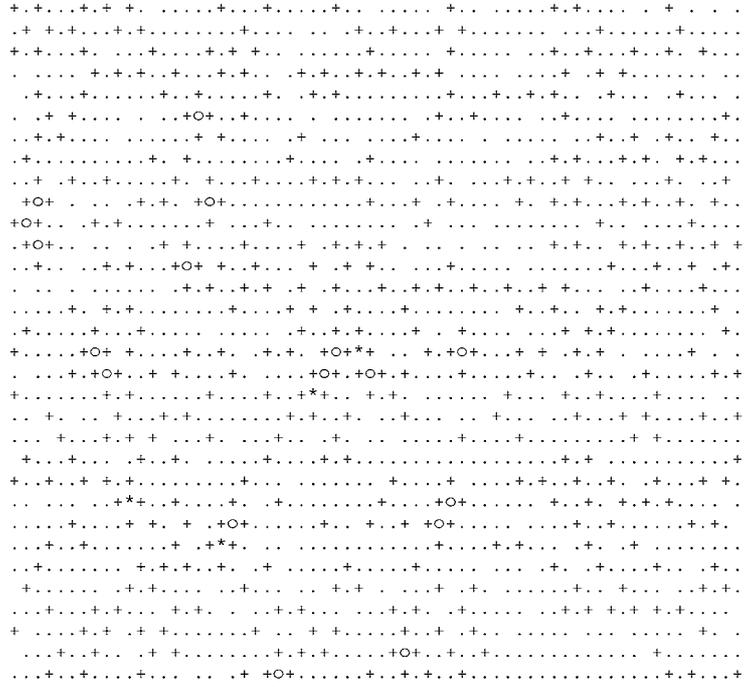
(b) If the colliding molecule is NO then its four neighbouring sites are also scanned for the presence of a vacancy. In the case that a second vacant site is available then step (2) takes place to produce two chemisorbed atoms N^{C} and O^{C} . In the case of the unavailability of a second vacant site, the nearest neighbourhood of NO^{C} is scanned for the presence of N^{C} in order to complete reaction step (3). All other simulation steps of model A are also valid for this model. In order to introduce desorption of NO, simulation step (a) is modified. If the randomly selected site is occupied by a NO molecule, it desorbs from the surface with some probability (d_{NO}). The values of d_{NO} lie between zero and one.

3. Results and discussion

The numerical results of this reaction system on a square lattice for a LH lattice model are already well known [4]. Here for a square lattice our model A shows two transition points y_1 and y_2 , between which the system has a SRS with continuous production of N_2 and H_2O . The values of y_1 and y_2 are 0.191 ± 0.001 and 0.207 ± 0.001 , respectively, showing a small window width of the order of ≈ 0.016 . For $y_{\text{H}} < y_1$ and $> y_2$, the surface is poisoned by a combination of O, OH, H, N and isolated vacancies. In the region of $y_{\text{H}} > y_2$, with the increase in y_{H}



(a)



(b)

Figure 3. Snapshots of the situation of a poisoned state of model A (without the diffusion of the species) when (a) $y_H = 0.25$ and (b) $y_H = 0.40$. The symbols +, *, o and blank space represent the N, OH, H, O and vacancies, respectively.

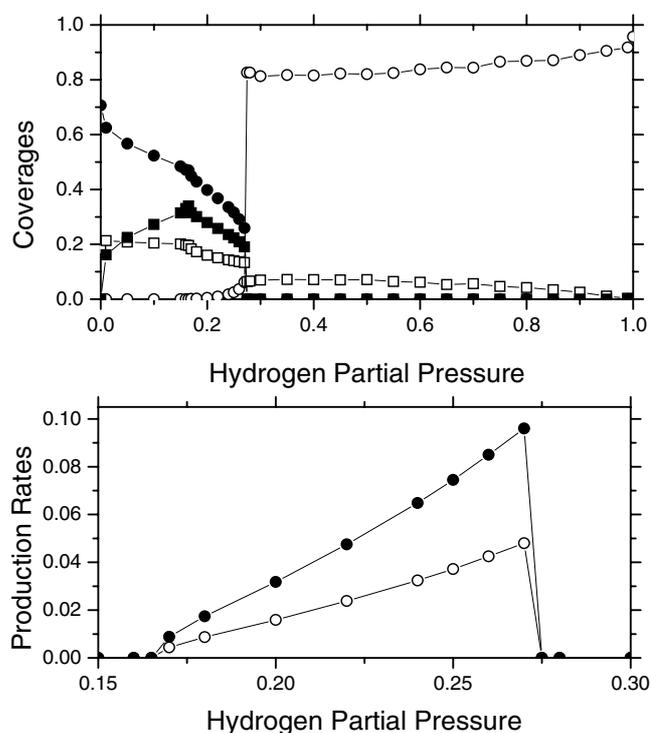


Figure 4. Coverages of O (full circle), H (open circle), N (open square) and OH (full square) plotted as a function of hydrogen partial pressure when diffusion of N atoms is considered in model A. The production rates (bottom) of H₂O (full circle) and N₂ (open circle) are plotted as a function of hydrogen partial pressure.

the coverages of O and OH become practically zero. On the other hand in this region, the coverage of H increases whereas that of N decreases with increase in y_H (figure 1). It is seen that H, OH and isolated vacancies are trapped between N atoms (figure 2). This shows that diffusion of N atoms may be more useful in order to widen the small reactive window. It is also important to note that the system gets into a poisoned state despite the fact that isolated vacancies are present and the H₂ molecule requires only one site to produce two precursors. This is because all the isolated vacancies present on the surface are trapped between N and H atoms (figure 3). If four N or H (an even combination of N and H) atoms surround a vacancy then, despite producing two precursors, a reaction cannot take place in the nearest neighbour (there is no reaction between N and H^P or H^C and H^P). Finally through reaction step (9) the two precursors are backscattered in the form of H₂(g).

Figure 4 shows the phase diagram when diffusion of N is introduced in model A. The diffusion of N widens the reactive window width. The values of y_1 and y_2 are 0.165 ± 0.005 and 0.275 ± 0.005 , respectively, showing a window width of the order of ≈ 0.11 . For $y_H < y_1$ ($y_H > y_2$), the surface is poisoned by a combination of O, OH and N (H and N). It is also important to note that this window width is almost the same (and is almost around the same region) as that observed by Khan *et al* [15] in the study of the NO–CO reaction when diffusion of N was introduced on a square surface. In the LH model of Yaldrum and Khan [4], with diffusion of N, continuous production of N₂ and H₂O starts when $y_H > 0.54$, whereas in this particular model diffusion of N starts the catalytic activity (with continuous production of

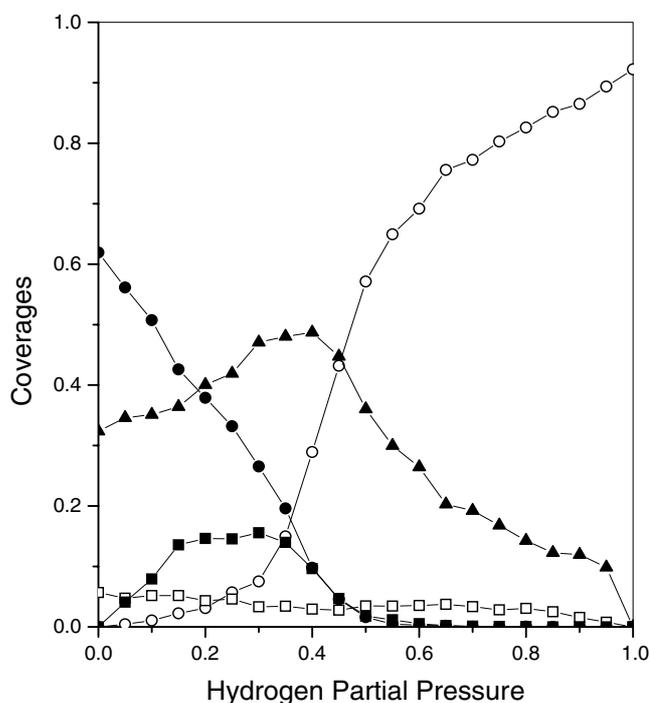


Figure 5. Coverages of O (full circle), H (open circle), N (open square), NO (full triangle) and OH (full square) plotted as a function of hydrogen partial pressure.

N₂ and H₂O) when $y_H > 0.165$. The other key difference in the two models is that a LH model (with N diffusion) gives a single transition point at $y_H > 0.54$ (catalytic activity continues until $y_H = 1.0$) whereas our model gives two transition points at $y_H = 0.165$ and 0.275 . The nature of these transition points is second order and first order, respectively. Therefore, our precursor model (along with N diffusion) gives a phase diagram, which is qualitatively similar to the ZGB model. The other key feature of our model is that, within the steady reactive region, the production rates of H₂O (R_{H_2O}) and N₂ (R_{N_2}) can be represented by simple mathematical equations of the type: $R_{H_2O} = 0.855(y_H) - 0.138$ (with standard deviation of the fit ≈ 0.0022) and $R_{N_2} = 0.427(y_H) - 0.069$ (with standard deviation of the fit ≈ 0.0012), respectively.

Figure 5 shows coverages of the species for model B. This situation is similar to that observed by Yaldram and Khan [4] when they studied the model along with the assumption that NO always adsorbs in dissociated form. In this situation, a significant number of N atoms were trapped between O, OH and H atoms in a similar way as that of the checkerboarding pattern of N atoms in the NO–CO reaction on a square surface. Therefore, the diffusion of N atoms in both reaction systems generates a reactive window. In our model A, again diffusion of a significant number of N atoms ($>20\%$) widens the reactive window from ≈ 0.02 to ≈ 0.11 . However, in figure 5, diffusion of a very small number of N atoms ($<3\%$) cannot generate any reactive window (figure 6). It has been checked and a phase diagram similar to figure 5 has been obtained when diffusion of N atoms was considered in model B. However, in the present case a large number of NO molecules are trapped between O, OH and H atoms. It is more likely that desorption of NO molecules (for which there is experimental evidence) may generate any reactive window. Figure 7 shows values of phase transition

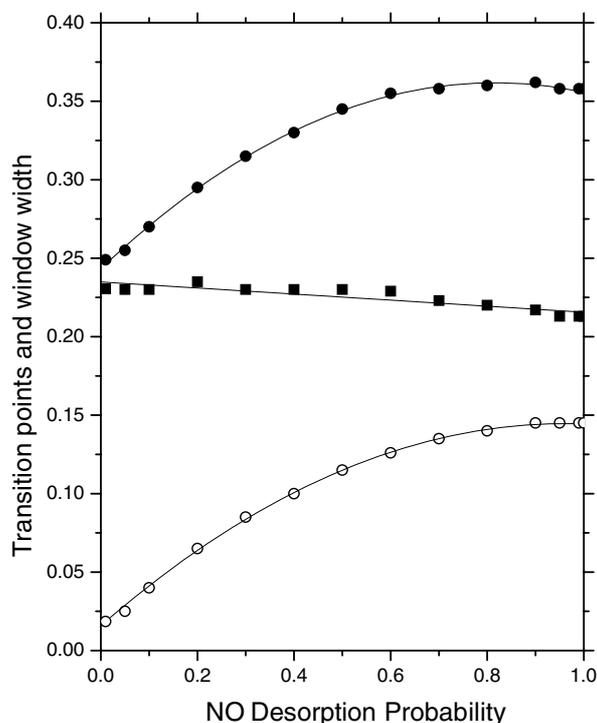


Figure 7. Transition points (y_1 and y_2) and reactive window width plotted as a function of NO desorption probability. Open and full circles represent the values of y_1 and y_2 , respectively. The full squares represent the window width. The fits of the data are also shown.

points (y_1 and y_2) along with reactive window width plotted as a function of NO desorption probability (d_{NO}). With an increase in d_{NO} , both y_1 and y_2 show behaviour of the type: $y_1 = 0.0159 + 0.268(d_{\text{NO}}) - 0.139(d_{\text{NO}})^2$ and $y_2 = 0.244 + 0.291(d_{\text{NO}}) - 0.178(d_{\text{NO}})^2$, respectively. The values of the standard deviation for the two fits are 0.0010 and 0.0015, respectively. Remarkably, the values of phase transitions shift (towards higher values of y_{H}) with d_{NO} but the width of the reactive window remains almost constant. The width of the reactive window fluctuates close to 0.23.

In a real experimental situation, the productive activity strongly depends upon temperature. Molecular NO desorption takes place with a maximum rate around 400 K when saturated surfaces are heated [28]. In our simulations the temperature has been involved in an indirect way by considering diffusion of the species and desorption of a NO molecule from the surface. With increase in temperature the desorption probability of NO increases and vice versa. In our opinion the inclusion of precursors to single lattice-gas non-thermal LH models leads to a better and more realistic description of heterogeneous catalyzed reactions. Consequently, further numerical and theoretical activity in this field will be very useful for the understanding of complex heterogeneous reactions.

4. Conclusions

The introduction of a precursor mechanism along the lines envisaged by Harris and Kasemo [22] adds some interesting features to the phase diagram of this catalytic reaction system. We have

studied two variants of the model. Model A is a dimer–dimer model, which assumes that NO is adsorbed in dissociated form on two vacant nearest-neighbouring sites whereas model B is a monomer–dimer model, which assumes that NO is adsorbed as a molecule on a single site. However, in model B NO may dissociate if another vacancy is available in the nearest neighbourhood of NO. The most striking feature of model A is the occurrence of a steady reactive region with continuous production of H₂O and N₂. The diffusion of N atoms widens the width of the reactive window. The qualitative nature of the phase diagram resembles that observed in the ZGB model for CO oxidation, despite the fact that the reaction scheme and adsorption rules are different in the two models. This shows that our model can lead the behaviour of the usual dimer–dimer reaction to a behaviour like the monomer–dimer reaction. Remarkably, in our model the dependence of reaction rate on y_H can be predicted through simple mathematical relations (linear fits) whereas the LH model of Yaldram and Khan [4] was unable to predict any such relation. When monomer–dimer adsorption rules (adsorption of NO on a single site) are followed in model B, the lattice gets poisoned for all values of y_H . In this poisoning NO plays the same role as that played by N in the dimer–dimer model of Yaldram and Khan [4]. It has been seen previously in LH models that diffusion of N atoms plays a crucial role in the generation of a steady reactive region [4, 5]. However, in model B the diffusion of N atoms does not generate a reactive window (due to the very small amount of N atoms on the surface). The situation becomes more interesting when desorption of NO from the surface is introduced in the model. Even a very small desorption probability ($d_{NO} \approx 0.01$) of NO generates SRS of width ≈ 0.23 . The qualitative nature of the phase diagram is similar to that of the ZGB model. The increase in d_{NO} does not increase the width of the reactive window. In the LH model of Yaldram and Khan [4] the width of the reactive window does not change with the diffusion probability of N. Therefore, desorption of NO in our model is playing the same role as played by N diffusion in the LH model of Yaldram and Khan [4]. However, it is interesting that the window width observed here (≈ 0.23) is exactly half of that observed in the LH model (≈ 0.46). In the LH model of Yaldram and Khan [4] diffusion probability of N atoms does not change the position of a single transition point whereas in our model B the desorption probability of NO shifts both y_1 and y_2 towards higher values of y_H . The shift of these points with an increase in d_{NO} can be shown mathematically by second-degree polynomial fits.

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