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Coupled diffusion on the $NO + H_2$ reaction on Pt(1 0 0): chemical wave pattern formation by defects

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Abstract

The catalytic reduction of nitric oxide by H_2 over the Pt(1 0 0) surface is studied as a function of partial pressures and diffusion of the reactants. Within the mathematical mean field model, originally proposed by Makeev and Nieuwenhuys [A.G. Makeev, B.E. Niewenhuys, Mathematical modeling of the $NO + H_2/Pt(1\ 0\ 0)$ reaction: "surface explosion", kinetic oscillations, and chaos, J. Chem. Phys. 108 (1998) 3740–3749], we incorporate the diffusion of adsorbed NO and H and the inhibitory site-blocking effect of adsorbed species N, O, NH, NH_3. By considering the influence of non-uniformities or defects, resulting in blocking or enhancing adsorption sites on the catalyst surface, the results show anisotropic front propagation with ellipsoidal shape in agreement with experimental results. The influence of the inert sites on global coupling as they are increased continuously is also studied.

Keywords: Adsorption; Kinetics; Mathematical; Modelling; Nonlinear dynamics

1. Introduction

The catalytic reduction of NO is important because the contaminant effects of NO in air [1]. The major reactions of NO conversion to nitrogen in the automotive catalytic converter are (Taylor [1]; Egelhoff [2]):

$$2NO + 2H_2 \rightharpoonup N_2 + 2H_2O$$

$$2NO + 2CO \rightharpoonup N_2 + 2CO_2$$

however this last step is too slow to provide a major path for NO reduction [2] and NO can also react to produce NH_3 :

$$NO + \frac{5}{2}H_2 \rightharpoonup NH_3 + H_2O$$

The selectivity of this reaction is governed by the temperature and the feed composition. These reactions were originally studied in polycrystalline systems but recently they have been studied on monocrystal of Pt(1 0 0) at low pressure because in this case the reactions can be considered isothermic. The extend of fundamental studies of NO reduction on single crystal surfaces has increased greatly in the last few years. The knowledge produced can provide a basis for proposing practical NO reduction catalysts.

Surface chemical reactions have a central role in the processes of heterogeneous catalysts, which are extensively used in chemical industry and environmental technology. In a catalytic process, the molecules of reactants are adsorbed from the gas phase onto a metal surface, diffuse on it, and react to form a product that goes back to the gas phase. Under certain circumstances these reactions can exhibit complex oscillations. Oscillations will not occur if the deviations from equilibrium are small and in this case the system can be described by linear relations. The oscillations occur due to feedback, either chemical (such as autocatalysis) or due to temperature (as in a non-isothermal reaction). Heterogeneous catalytic reactions satisfy the necessary requirements for the appearance of auto-oscillations because the continuous mass flow of reactants and heat exchange with the surroundings. The

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Nomenclature

D_i	diffusion coefficient of chemisorbed species without influence of other coadsorbed species ($m^2\,s^{-1}$);
D_{ij}	diffusion coefficient of specie i influence by coverage of specie j;
I_α	lateral interactions;
k_i	reaction rates;
L	characteristic length of catalyst;
p_{NO}	NO partial pressure (bar);
p_{H_2}	H_2 partial pressure (bar);
$R_d = D_y/D_x$	diffusivity relationship
R_i	rates of elementary reaction steps;
S_i	sticking probabilities (i = NO, H_2);
T	catalyst temperature (K);
t	time (s)
Greek letters	
ϵ_{ap}	parameters of lateral interactions;
θ_i	fractional coverage of chemisorbed species, (i = NO, H, N, O, NH, NH_3);
θ_*	fraction of free adsorption sites;
α, β, δ	effective phenomenological parameters for inhibated adsorption

flux of energy and matter through the open system maintain it far from equilibrium and temporal and spatial organization become possible.

The occurrence of kinetic oscillations during the catalytic reduction of NO with either CO or H_2 [3–9], have been observed and found to occur for gas reactant pressures in the range 10^{-6} to 10^{-5} mbar in the range of temperatures from 430 to 500 K. These reactions show complex dynamical behavior as pattern formation and chaotic behavior. The review by Imbihl [10], Imbihl and Ertl [11] and Slinko and Jaeger [12] on a large number of catalytic reactions are very instructive.

To describe the occurrence of kinetic oscillations, Cobden et al. [6] have proposed a "vacancy" mechanism to explain the kinetic oscillations. In this "vacancy model" the oscillations are due to autocatalytic surface reaction, which increase the number of vacant sites for NO dissociation. Later, Makeev and Niewenhuys [13] have developed a mathematical model to prove that autocatalysis of NO decomposition by vacant sites is one of the main properties that keeps the system oscillating. A very important ingredient of this model is the coverage dependency of the activation energies for NO and CO desorption. So, in this model the system presents oscillatory behavior without involvement of the surface structural transformation, $hex \rightharpoonup 1 \times 1$, which takes place on Pt surfaces due to the presence of adsorbates and has been showed to be important for other chemical oscillations such as in NO + CO [3]. So, it can be considered that oscillations for the NO + H_2/Pt(1 0 0) reaction take place on a surface that is completely in the 1×1 structure.

The interplay and synchronization between reaction kinetics and diffusion can produce a rich variety of spatial patterns in surfaces, especially due to the anisotropy of diffusion in surfaces. Furthermore, diffusion of adspecies can vary in several orders of magnitude. The traditional approach for considering diffusion is adding terms which obey Fick's second law with constant diffusion coefficients to the equations describing the kinetics. In a reaction-diffusion system, the concentrations C_i of the chemical species are described by the following partial differential equation (PDE)

$$\frac{\partial C_i}{\partial t} = f(\ldots C_j, \ldots) + D_i^0 \bigtriangledown^2 C_i$$

where D_i^0 is the diffusion coefficient for the ith substance and f_i specifies the reaction mechanism. In a recent paper we have taken such approach for the NO + H_2 reaction on Pt(1 0 0) [14] on a two dimensional lattice and showed that differences in the diffusivity in the x and y directions change the oscillation periods. But this approach ignores the influence of coadsorbed species in diffusion and front propagation is not observed.

Steps and other mesoscopic surface defects have also a considerable influence on the course of the reactions. Steps and kinks are also called line defects, to distinguish them from atomic vacancies, or adatoms, which are called point defects. These point defects are present in most surfaces and are important participants of atom transport along the surface (surface diffusion), although their equilibrium concentrations are much less than 1% of a monolayer. Defects will make synchronization more difficult which causes a breakdown of global coupling, leading from spatially uniform oscillations to the formation of wave patterns.

Interest in the effect that site blocking has on catalytic reactions stems from its occurrence in real systems. For example in catalytic converters inert species, such as sulphur, deposit on the catalyst surface during the exhaust of the combustion gases. These inert species cause the active sites to be non-reactive and also block potential adsorption sites on the catalyst surface. This lead to inefficiencies in the system. Crystal defects produced on the catalyst surface also result in non-binding or blocked sites.

In this paper we make an study of the NO + H_2/Pt(1 0 0) reaction, incorporating a realistic description of diffusion by considering site blocking effects for NO and hydrogen diffusion by the coadsorbed species. We also consider the influence of defects, considered here as blocking inert sites for the NO adsorption. Our investigation began by studying the effect that a single inert defect has on the local environment and we made the center point of the lattice a defective site. Then we study the scenario which develops in a medium as the influence of defects is continuously increased. For the elementary reaction steps we use the model proposed by Makeev and Nieuwenhuys [13], which reproduces very well the experimental observations of regular and chaotic oscillations of the NO+H_2/Pt system and our treatment of chemical diffusion follows the formulation by Makeev and Imbihl [14,15].

2. Model

2.1. kinetic equations

The following set of elementary step have been formulated for the NO+H_2 reaction on Pt(1 0 0) [13]:

$$NO(g) + * \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NO_{ads} \quad \text{(R1 and R2)}$$

$$H_2(g) + 2* \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 2H_{ads} \quad \text{(R3 and R4)}$$

$$NO_{ads} + * \underset{k_6}{\overset{k_5}{\rightleftharpoons}} N_{ads} + O_{ads} \quad \text{(R5 and R6)}$$

$$2N_{ads} \overset{k_5}{\rightleftharpoons} N_2(g) + 2* \quad \text{(R7)}$$

$$O_{ads} + H_{ads} \overset{k_8}{\rightleftharpoons} OH_{ads} + * \quad \text{(R8)}$$

$$N_{ads} + H_{ads} \underset{k_{10}}{\overset{k_9}{\rightleftharpoons}} NH_{ads} + * \quad \text{(R9 and R10)}$$

$$NH_{ads} + H_{ads} \overset{k_{11}}{\rightharpoonup} NH_{2,ads} + * \quad \text{(R11)}$$

$$NH_{3,ads} \overset{k_12}{\rightharpoonup} NH_3(g) + * \quad \text{(R12)}$$

$$NH_{2,ads} + H_{ads} \overset{k_13}{\rightharpoonup} NH_{3,ads} + * \quad \text{(R13)}$$

$$OH_{ads} + H_{ads} \overset{k_14}{\rightharpoonup} H_2O_{ads} + * \quad \text{(R14)}$$

$$H_2O_{ads} \overset{k_15}{\rightharpoonup} H_2O(g) + * \quad \text{(R15)}$$

where * denotes a free adsorption site of the Pt(1 0 0)-(1 × 1) surface; NO(g), H_2(g) are the reactants in the gas-phase with partial pressures p_{NO} and p_{H_2}, respectively. In the last Eqs. (R1 and R2) account for NO adsorption and desorption, (R3 and R4) for H adsorption and desorption, (R5 and R6) for NO dissociation, (R7) for N desorption, (R8) for OH formation, (R9 and R10) for NH formation, (R11) for NH_2 formation, (R12) for NH_3 desorption, (R13) for NH_3 formation, (R14) for H_2O formation and R15 for H_2O desorption. The reaction products are N_2(g), NH_3(g) and H_2O(g). The surface coverage are denoted by $(NO)_{ads}$, $(H)_{ads}$, $(N)_{ads}$, $(O)_{ads}$, $(NH)_{ads}$,and $(NH_3)_{ads}$.

The desorption of $(H_2O)_{ads}$ and the hydrogenation of intermediates $(OH)_{ads}$ and $(NH_2)_{ads}$ are assumed to be fast processes. In consequence, only six species are considered (in the following equations the surface coverage are denoted by θ_p, p = NO, H, N, O, NH, NH_3). The non-ideality of the adsorbed layer is taken into account through lateral interactions ϵ_{ap}, specified below. This quantity reflects microscopically the influence of the local environment on the activation energies of the elementary reaction steps and can be considered as the difference of the lateral interactions in the activated and ground states. The following coupled ordinary differential equations (ODE's) describe the kinetics of the reaction:

$$\frac{d\theta_{NO}(t)}{dt} = R_1 - R_2 - R_5 + R_6 = f_{NO} \tag{1}$$

$$\frac{d\theta_{H}(t)}{dt} = 2R_3 - 2R_4 - 2R_8 - R_9 + R_{10} - 2R_{11} = f_H \tag{2}$$

$$\frac{d\theta_{N}(t)}{dt} = R_5 - 2R_7 - R_6 - R_9 + R_{10} \tag{3}$$

$$\frac{d\theta_{O}(t)}{dt} = R_5 - R_6 - R_8 \tag{4}$$

$$\frac{d\theta_{NH}(t)}{dt} = R_9 - R_{10} - R_{11} \tag{5}$$

$$\frac{d\theta_{NH_3}(t)}{dt} = R_{11} - R_{12} \tag{6}$$

R_i are the rate of the elementary steps (R1–R12) given above :

$$R_1 = k_1 p_{NO} S_{NO} \theta_e, \qquad R_2 = k_2 \theta_{NO} I_2$$

$$R_3 = k_2 p_{H_2} s_{H_2} (\theta_e)^2, \qquad R_4 = k_4 (\theta_H)^2 I_4$$

$$R_5 = k_5 \theta_{NO} \theta_e I_5, \qquad R_6 = k_6 \theta_N \theta_O$$

$$R_7 = k_7 (\theta_N)^2 I_7$$

$$R_8 = k_8 \theta_O \theta_H$$

$$R_9 = k_9 \theta_N \theta_H, \qquad R_{10} = k_{10} \theta_{NH} \theta_e$$

$$R_{11} = k_{11} \theta_{NH} \theta_H$$

$$R_{12} = k_{12} \theta_{NH_3}$$

where

$$\theta_* = 1 - \theta_{NO} - \theta_H - \theta_N - \theta_O - \theta_{NH} - \theta_{NH_3}$$

$$k_\alpha = \nu_\alpha \exp[-E_\alpha/(RT)], \alpha = 1, \dots 12$$

$$I_\alpha = \left\{ \theta_* + \sum_{p=1}^{6} \theta_p \exp[\epsilon_{\alpha p}/(RT)] \right\}^{m_\alpha}$$

θ_* is the fraction of empty sites available for adsorption; m_α, the number of nearest-neighbor sites; and S_i is the sticking coefficient.

The factor I_α takes into account the influence of lateral interactions in the framework of the lattice-gas model for a well mixed ad layer. When there is no such lateral interactions $\epsilon_{\alpha p} = 0$ and $I_\alpha = 1$. The kinetic parameters given in Table 1

Table 1
The energy and bare frequency parameters that enter the expression for the various rate constants $k = \nu \exp(-E/RT)$

Reaction step (α)	$\nu_\alpha(\mathrm{s}^{-1})$	E_α (kcal/mol)
1	$2.14 \times 10^5\ \mathrm{mbar}^{-1}$	0
2	$1.7 \times 10^{15}\ \mathrm{mbar}^{-1}$	37
3	$8.28 \times 10^5\ \mathrm{mbar}^{-1}$	0
4	10^{12}	25
5	2×10^{15}	28
6	2×10^{15}	23
7	10^{13}	24
8	10^{13}	13
9	10^9	15
10	10^{13}	29
11	10^9	17.7
12	10^9	19

$S_{\mathrm{NO}}k_1 = 1.93 \times 10^5(\mathrm{mbar}^{-1}\mathrm{s}^{-1})$, $S_{\mathrm{H}_2}k_3 = 1.656 \times 10^5\ (\mathrm{mbar}^{-1}\mathrm{s}^{-1})$.

are the same used in our previous work [14]. The parameters for lateral interactions were taken from this last reference and are $|\ \epsilon_{\alpha,i}\ | < 2$.

2.2. Spatially distributed model

For describing spatial pattern formation we must incorporate surface diffusion into the above equations. As mentioned earlier we will follow the formulation given by Makeev and Imbihl [15,16] where coverage-dependent diffusion coefficients are considered. We will consider only two diffusing species, NO and H, because they are more mobile than the other species [15,16].

The following set of differential equations will describe the global behaviour of our system:

$$\frac{\partial \theta_{\mathrm{NO}}}{\partial t} = -\nabla J_{\mathrm{NO}} + f_{\mathrm{NO}}(\theta_i, \theta^*, I) \tag{7a}$$

$$\frac{\partial \theta_{\mathrm{H}}}{\partial t} = -\nabla J_{\mathrm{H}} + f_{\mathrm{H}}(\theta_i, \theta^*, I) \tag{7b}$$

Here f_{NO} and f_{H} are the right-hand side of Eqs. (1) and (2), respectively. For the other species we have

$$\frac{\mathrm{d}\theta_{\mathrm{j}}}{\mathrm{d}t} = f_i(\theta_i, \theta_i^*, I) \tag{7c}$$

where j = N, O, NH, NH_3 and the f_i are the corresponding right-hand sides of Eqs. (3)–(6).

The reaction kinetics is contained in f_i and the diffusive fluxes, $\mathbf{J}_{\mathrm{K}}$, for species K = NO, H, must be prescribed in terms of the species coverage and their gradients in order to close the above equations. Note that if $\mathbf{J}_i = -D_i \nabla \theta_i$ the equations reduce to the Fickean case. In general, the diffusive fluxes, $\mathbf{J}_{\mathrm{K}}$ of the diffusing species NO and H are related to their infinitesimal coverage gradients by [17] :

$$\begin{pmatrix} J_{\mathrm{NO}} \\ J_{\mathrm{N}} \end{pmatrix} = -\begin{pmatrix} D_{\mathrm{NO,NO}} & D_{\mathrm{NO,H}} \\ D_{\mathrm{H,NO}} & D_{\mathrm{H,H}} \end{pmatrix} \begin{pmatrix} \nabla \theta_{\mathrm{NO}} \\ \nabla \theta_{\mathrm{H}} \end{pmatrix} \tag{8}$$

Table 2
Difussion constants used in the simulation

Specie	D_i^0 (cm^2/s)	E_i (kcal/mol)	α	β	δ
NO(x)	1.00×10^{-3}	3500	1.0	1.0	0.01
NO(y)	3.85×10^{-3}	3500	1.0	1.0	0.01
H(x)	0.25×10^{-6}	3500	1.5	1.1	0.01
H(y)	1.00^{-6}	3500	1.5	1.5	0.01

where the entries of this matrix or tensor are the chemical diffusion coefficients which are coverage dependent. Unfortunately, there are not reported values for the D_{ij} coeficients. Makeev and Imbihl [15,16] have proposed a procedure where these quantities are calculated. For each diffusing species they take into account that the other coadsorbed species may effectively block vacant sites for diffusion. In two dimensions, the reaction-diffusion model is represented by a system of two PDE's which substitute Eqs. (7a) and (7b) for NO and H:

$$\frac{\partial \theta_{\mathrm{A}}}{\partial t} = D_{\mathrm{A}} \left\{ \theta_{\mathrm{A}}^* \frac{\partial^2 \theta_{\mathrm{A}}}{\partial x^2} + \theta_{\mathrm{A}} \frac{\partial^2 \theta_{\mathrm{A}}^*}{\partial x^2} + R_d \left[\theta_{\mathrm{A}}^* \frac{\partial^2 \theta_{\mathrm{A}}}{\partial y^2} + \theta_{\mathrm{A}} \frac{\partial^2 \theta_{\mathrm{A}}^*}{\partial y^2} \right] \right\} + f_i \tag{9}$$

A = NO, H and for the other species, Eq. (7c) holds. The two-dimensional reaction-difussion equations contains thus second order spatial derivatives both for the adsorbate coverages as well as for the concentration of vacant sites θ_{A}^*, vailable for the adsortion of species A which are given by:

$$\theta_{\mathrm{A}}^* = \max\{(1 - \theta_{\mathrm{NO}} - \alpha_{\mathrm{A}}\theta_{\mathrm{H}} - \alpha_{\mathrm{A}}\theta_{\mathrm{N}} - \beta_{\mathrm{A}}\theta_{\mathrm{O}} - \theta_{\mathrm{NH}} - \theta_{\mathrm{NH_3}}), \delta_{\mathrm{A}}\} \tag{10}$$

the parameters α, β, δ are effective phenomenological parameters estimated by fitting simulations to experiments and are given in Table 2. The diffusion coefficients are calculated by the Arrhenius form :

$$D_{\mathrm{A}} = D_{\mathrm{A}}^0 \mathrm{e}^{-E_{\mathrm{A}}/RT} \tag{11}$$

D_{A}^0 and E_{A} are also given in Table 2. We take the anisotropy in the x and y directions, D_x, D_y, in the ratio (1:3.85) for NO and that for H the ratio (1:4), based on information from Refs. [14–16], respectively. Numerically, we have used Gear's method [18] for solving stiff ODE's, which provides efficiency and accuracy of integration.

3. Results

3.1. One defect

In general, we will consider the defect as represented as an inert node at the central part of the lattice, where the sticking coefficient S_{NO} for NO is cero (inert site). As was mentioned before interest in the effect that site blocking has on catalytic reactions stems from its occurrence in real systems. Inert species can deposit on the catalyst cand cause the catalyst sites to be non-reactive and also block potential adsorption sites.

The catalytic surface is represented by a square lattice of size 11 × 11 nodes with periodic boundary conditions, representing a 0.025 cm × 0.025 cm crystal. The surface non-uniformity is modeled by assuming different sticking coefficient of NO on the surface of the catalyst caused by the large sensitivity of the adsorption rate on surface dislocations. We will consider the defect as represented as an inert node at the central part of the lattice, where the sticking coefficient S_{NO} for NO is cero (inert site). We make the assumption that the blocking site only affects the NO adsorption, but we have also performed calculations for $S_{NO} \neq 0$ to show the similar result that results when the defect enhances the adsorption. In this way the defect plays a role of a selective adatom only on NO adsorption. The effect of H_2 adsorption on this defect will be commented later. At the other sites of the lattice the adsorption and kinetic constant for all species are given by Table 1. We must state here that there is a dependence of activation energy on coverages. Such dependence is related with surface heterogeneity [1]. In general, coverage-dependent activation energies arise if energetic interactions between adparticles exist. In our calculations we have considered this only through I_α, and have not attempted to consider more elaborated mechanisms, for example that at low temperatures the catalytic sites are blocked by some species and with increasing temperature, and either due to adsorption or reaction, the blocking species are removed. To solve Eqs. (7)–(11) we use the method of lines in which one discretizes the diffusion term and solve the ODE across a whole line in space at each time step. In total 246 stiff ODE's are solved by the Gear method [18].

It was shown in previous investigations [13,14] that changing the governing parameter $R_p = p_{H_2}/p_{NO}$ at constant T the transition to aperiodicity occurs via the Feigenbaum scenario, that is, period-doublings. To observe the period doubling, in our present simulations with coupled diffusion we change again the governing parameter R_p. In the next figures we show the oscillatory behaviour in the NO coverage averaged over the whole crystal, $\theta_{NO,av}$, and also the behaviour of θ_{NO} across the crystal. All the calculations were performed at $T = 457$ K, which is among the range of the experimental studies by Rausemberger et al. [19,20].

First, it is observed now that there is a chemical propagation around the defect with a mountain landscape for the NO coverage with respect to its mean value. This has the shape of an ellipse when projected on the x–y plane, which change with time, stretching and contracting which means that the mountains grow and decrease in size with time.

This is shown in Fig. 1, where a sequence of snapshots are shown for times t = 54–57 s (see inset) around the maximum in $\theta_{NO,av}$. The conditions correspond to the case where the system shows period four (P4) oscillations. At $t = 54$ s the ellipse is developed, propagates and in $t = 56$ s shows its largest development, corresponding to the maximum in $\theta_{NO,av}$. Then it contracts as $\theta_{NO,av}$ decreases (Fig. 1d, $t = 57$ s) and for $t = 62$ s (Fig. 1e) shows a minimum size and the cycle begins again. In order to compare with these results we have performed calculations with $S_H = 0$, that is, the central site is also inert to hydrogen adsorption. The results in this case (not shown) is that the oscillations die very soon (rougly around $t \sim 50$ s), and the stationary state is attained. In conclusion, if there is one inert site, both for NO and H_2 adsorption, there are not sustained oscillations. We must remark here that this kind of results (damping effect observed in the oscillations in absence of purity) has been demonstraded experimentally in the NO + CO/Pt(1 0 0) reaction [3].

If we have an enhanced adsorption, different sticking coefficient of NO on the surface of the catalyst caused by the large sensitivity of the adsorption rate on surface dislocations, a similar disturbation propagates along the crystal but now a protuberance is created at the center of the crystal, where the defect is located. This is shown in Fig. 2 for different times. At $t = 50$ s (Fig. 2a) there is a small disturbance which corresponds to $\theta_{NO,av} = 0.093$. As $\theta_{NO,av}$ increases to a value 0.271 the disturbance grows and the wave propagation is extended (Fig. 2b). Finally at the maximun of the cycle, $\theta_{NO,av} = 0.391$ and the propagation reaches its larger extension. Then the cycle begins again. We see that this case is very similar to that of the inert defect, exept that in this last case there is a vacancy at the center of the lattice due to the null adsorption of NO.

We consider now the effect of variation of R_p in the case of one inert defect. Fig. 3a–d (left column) shows time series for decreasing values of R_p, different oscillatory periods are observed. Period-1 (P1) oscillations are shown for $p = 2.58$(d); period-2 (P2)oscillations for $p = 2.518$(c); period-4 (P4) oscillations for $p = 2.516$ (b). Chaos is developed for $p = 2.512$ (a). The right columns of Fig. 2 show θ_{NO} for each of the maximal amplitude of the corresponding period (noted with dots in the left Fig. 1), that is, they show the behaviour of the NO coverage in their maximum value. It is also shown the projection on the $x - y$ plane. The main result here is that in effect, there is a period doubling as R_p is decreased and the chemical perturbation creates crests and valleys ("mountains"), or an ellipse on the plane xy. The bigger the value of $\theta_{NO,av}$ the bigger the size of the corresponding ellipses, as in Fig. 3d. Another important feature is that the presence of this defect destabilizes the system and the period eight (P8) is not observed as was the case in the homogeneous treatment [14]. It is important to notice that in most experimental studies of period-doubling behaviour, the P8 is not observed. This has been currently attributed to noise. We suggest here that this can also be attributed to imperfections in the crystal.

In conclusion, the presence of one defect inhibiting or enhacing the adsorption of NO creates a point of propagation of a disturbance with an ellipsoidal shape when projected onto the xy plane. This propagation attains its maximum propagation at the maximum of NO coverage.

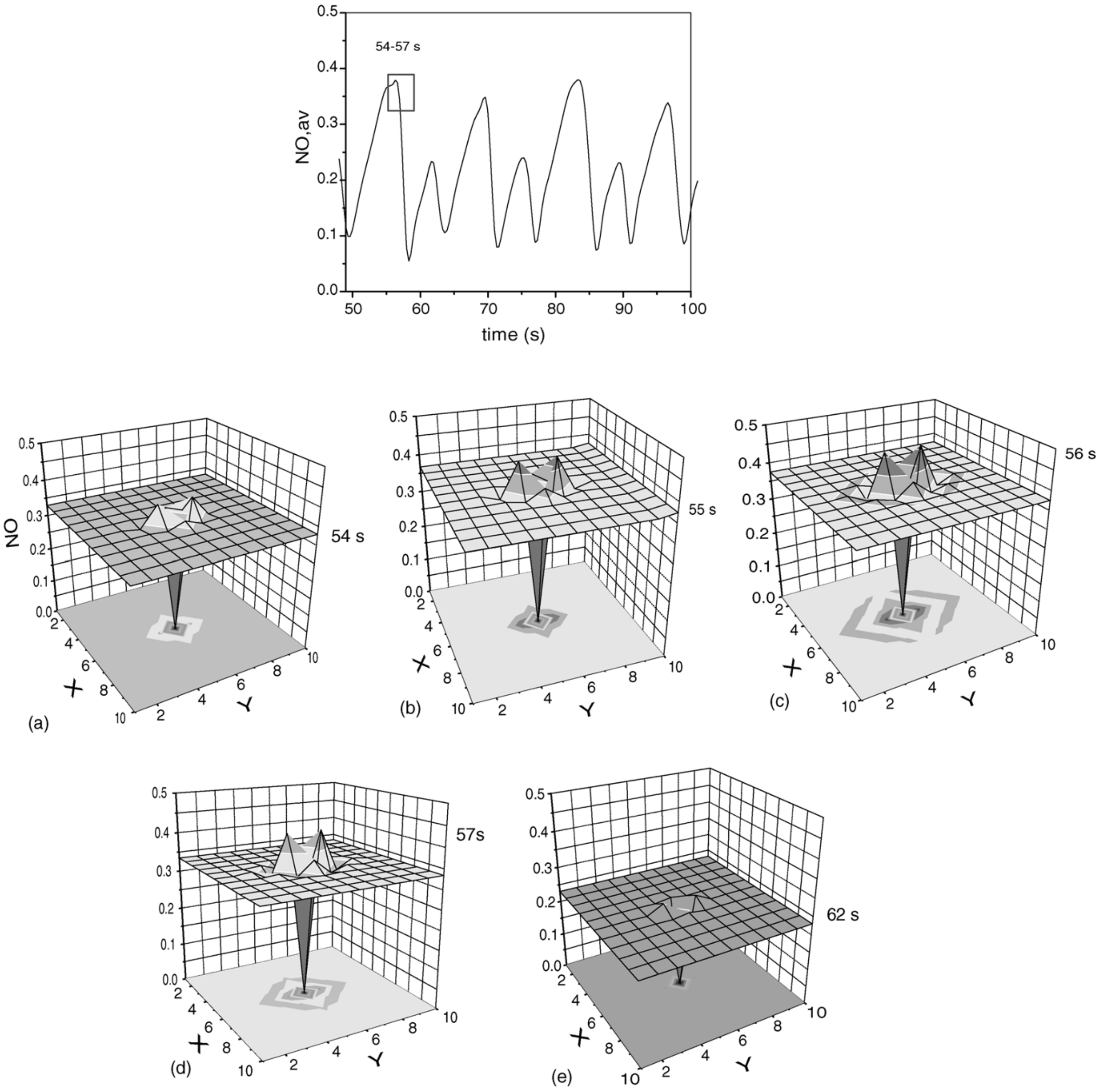

Fig. 1. Development of the chemical disturbance due to the presence of one inert defect, where $S_{NO} = 0$. (a) $t = 54$ s, (b) $t = 55$ s, (c) $t = 56$ s, (d) $t = 57$ s, (e) $t = 62$ s. $T = 457$ K, $p_{NO} = 1.1 \times 10^{-6}$ mbar and $p_{H_2} = 7.6 \times 10^{-6}$ mbar.

3.2. Multiple defects

In the experimental reports by Rausemberger et al., (1996,1998) the formation of multiple ellipses are observed. This can be attributed to the presence of multiple defects. Because the relatively small size of the lattice considered here, we have studied only the influence of few inert defects. We have taken as the initial condition a period four (P4). Fig. 4a–d shows time series (left) and the formation of ellipses on the *xy* plane, the snapshots are taken at the maxima of the oscillations and represents thus the largest expansion of these ellipses as was established before. First note that on increasing the number the defects the concentration of NO is smaller and the ellipses will have lesser extensions. So increasing the number of defects causes the number of periods to decrease. With three defects the system is P2 (Fig. 4b), with four is P1 (Fig. 4c) and with five defects a stationary state is attained (Fig. 4d). Surprisingly, the addition of two defects destabilizes the system and aperiodic oscillations are obtained (Fig. 4a). This can be ex-

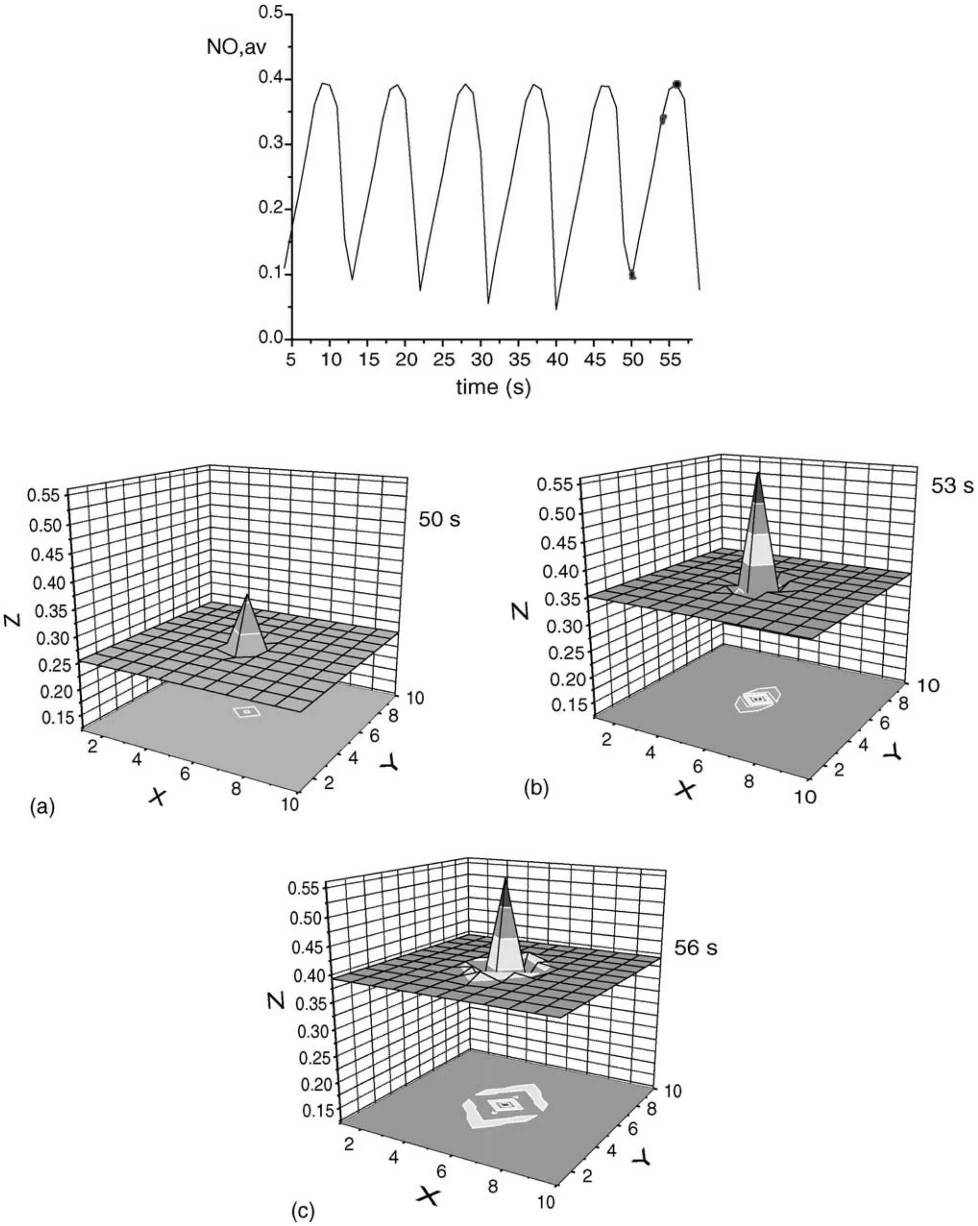

Fig. 2. Development of the chemical disturbance due to the presence of one defect with $S_{NO} \neq 0$ (a) $t = 54$ s, (b) $t = 55$ s, (c) $t = 56$ s, (d) $t = 57$ s, (e) $t = 62$ s. Same conditions as in Fig. 1.

plained by considering that with only two defects the concentration of NO is higher and there is a possibility to the perturbations to collide as is shown in Fig. 4a. With more defects the ellipses do not reach each other, as is shown in Fig. 4b–d. In this way, the interaction of perturbations destabilizes the system and it becomes chaotic. To prove this we have increased the lattice size in order to consider the two defects more distant apart. We have verified that in this case the defects do not interact, the perturbations die before they reach each other and P4 is maintained (the picture is not shown). In conclusion, the interference of defects can destabilize the periodic behaviour and the system becomes aperiodic.

We must note that in our calculations the size of the crystal is rather small, 0.025 cm × 0.025 cm, because our computer limitations. In this way we have considered only five defects, but it represents 5% of the avaiable sites. This is a rather small fraction. Unfortunatly, there is no experimental data to which compare. But comparaisons with other calculation can be made. For example, for an homogeneous treatment of the NO + H_2 reaction [14], the oscillations died when a fraction of around 8% of the sites are inert. In relation with different authors, the more studied reaction has been the oxidation of CO on Pt surfaces. For example, in 1992, Hovi et al. [21] conducted a Monte Carlo-type study of the Ziff–Goulari–Barshad (ZGB) model and found that the first-order

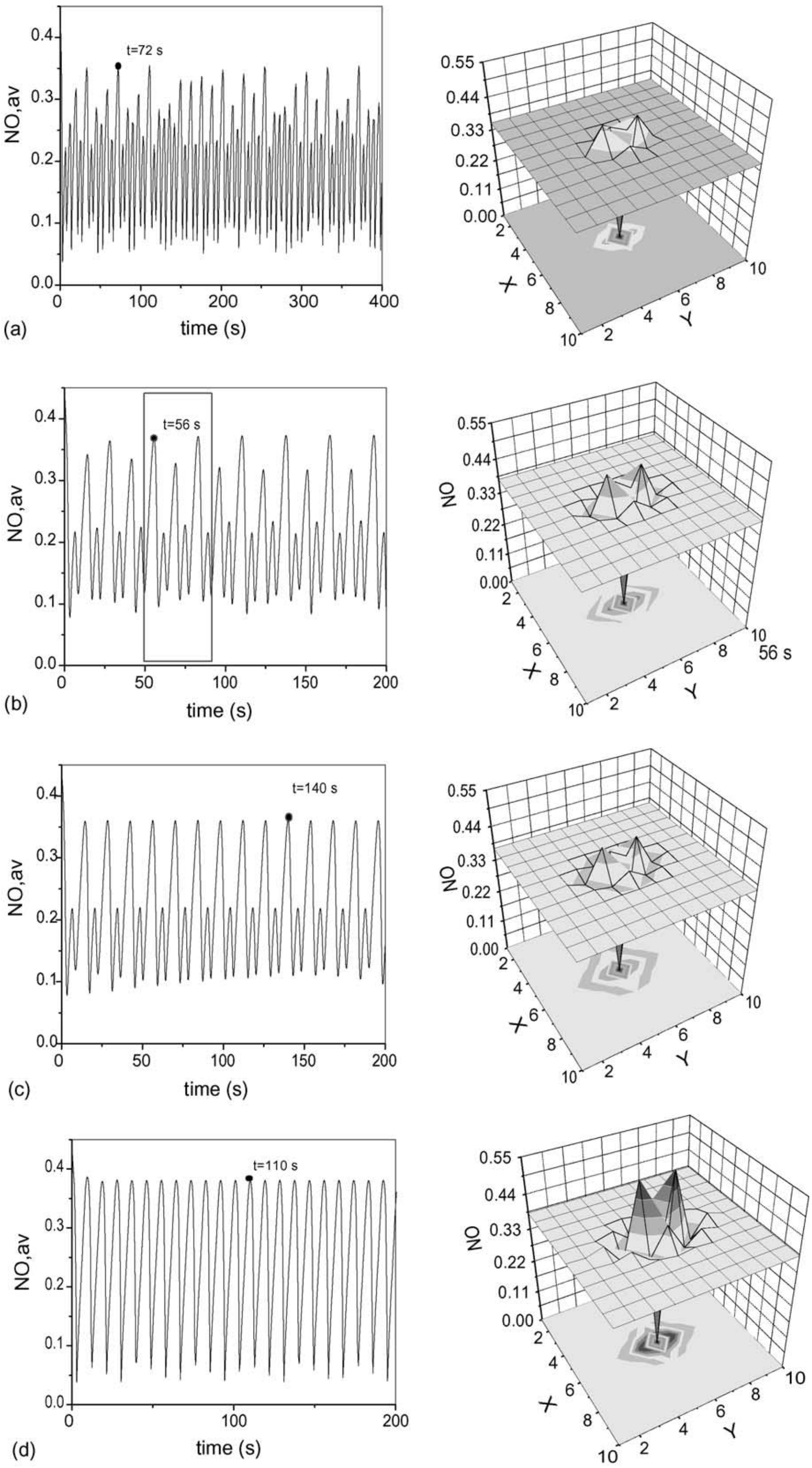

Fig. 3. Period-doubling route to chaos in $\theta_{NO,av}$ as a function of time for different values of the pressure ratio $R_p = P_{H_2}/p_{NO}$. Left : (d) period-1, $R_p = 2.58$. (c) period-2,$R_p = 2.518$. (b) period-4, $R_p = 2.516$. (a) Chaos, $R_p = 2.512$. The right colums are NO coverage taken at the maximum of the amplitudes, shown as dots in the corresponding left figures. The planes represent $\theta_{NO,av}$.

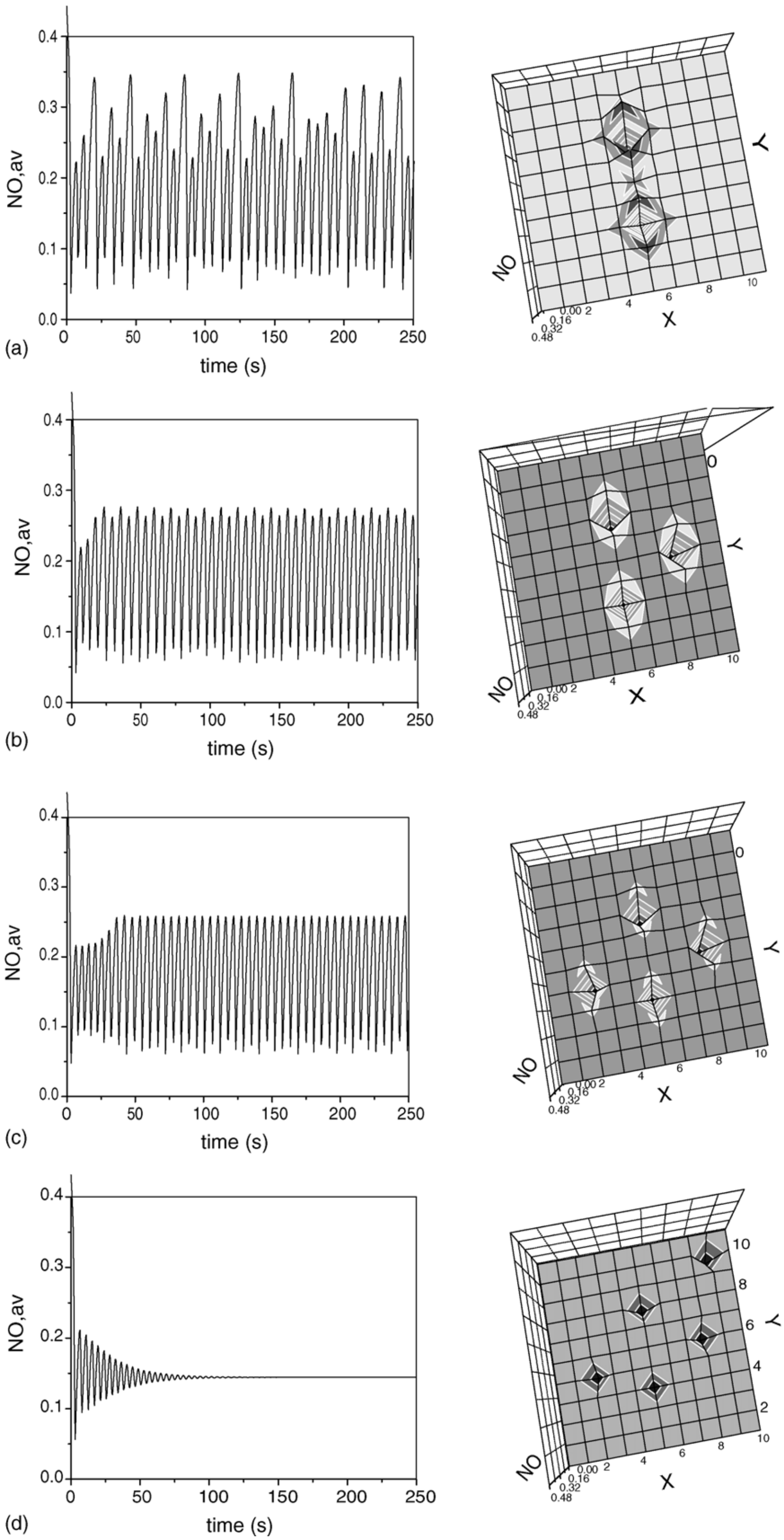

Fig. 4. Effect of increasing the number of inert defects in a square lattice. (a) Two-defects (placed next to each other) and chaos (left), (b) three defects and period-2(left), (c) four defects and period-1(left), (d) five defects and stationary state(left). Explanation in the text.

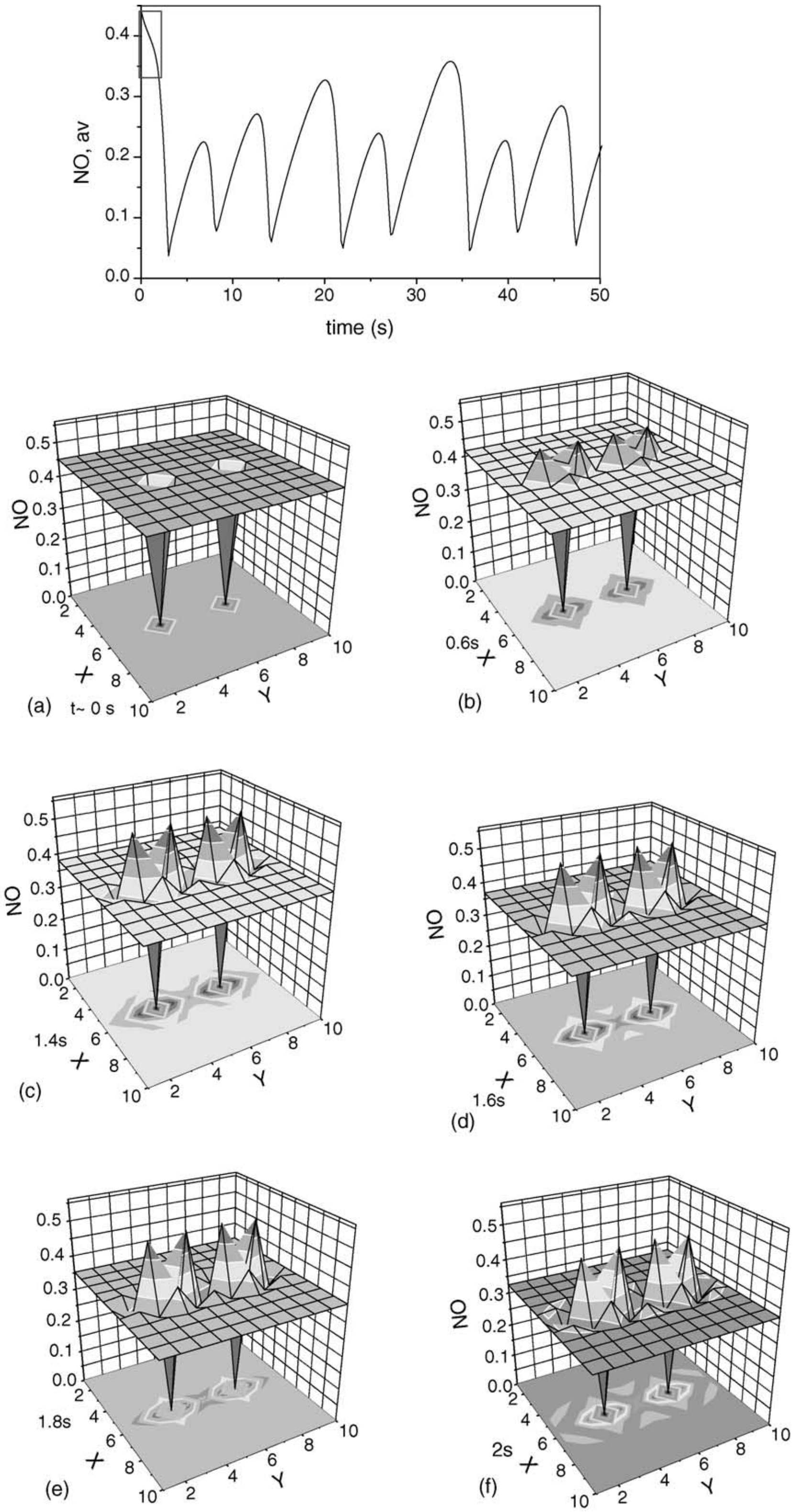

Fig. 5. Propagation of concentration fronts. The snapshots correspond to : (a) $t = 0$ s, (b) $t = 0.6$ s, (c) $t = 1.4$ s, (d) $t = 1.6$ s, (e) $t = 1.8$ s, (f) $t = 2.0$ s.

CO poisoning transition appears to become continuous when more than 8% of the surface is covered by defective sites placed in a random arrangement. This poisoning of the crystal surface CO can stop the reaction. So, there is theoretical evidence that even a small fraction of impurities can change dramatically the catalytic reaction.

3.3. *Collision between propagating fronts*

As was mentioned above the interaction between two propagating fronts desynchronize the oscillations and the system becomes chaotic. We have considered this in more detail by solving numericaly the equations and following the evolution at closed time intervals. The collision of two propagating fronts is shown in Fig. 5a–e, where it is observed how the propagating fronts generate from two defects (Fig. 5 $t \sim 0$ s), approach (Fig. 5b, $t = 0.6$ s), collide (Fig. 5c $t = 1.4$ s), interfere constructively (Fig. 5d and e, $t = 1.6, 1.8$ s) and begin to relaxe (Fig. 5f, $t = 2$ s) until the perturbation disappear and the cycle begins again. The perturbations are continuously formed because the presence of defects and because the adsorption and reaction of species (NO, H, . . .) are taking place continuously. In a certain way they remind us the interactions of two waves on a liquid surface, such as waves on the surface of water, but they are much more complex as the composition (coverage) of the medium is changing continuously. A mathematical treatment of this subject is beyond the scope of the present work.

4. Conclusion

Within the mathematical MF model proposed in Ref. [13] for the kinetics of the NO + H_2 reaction on Pt(1 0 0), and extended in our previous study [14], a realistic description of diffusion of species NO and H, has been incorporated now. This description considers the inhibitory site-blocking effect of co-adsorbed species N, O, NH, NH_3. The presence of inert defects (where there is no adsorption) or dislocations (where the adsorption rate is enhanced) trigger a propagating chemical wave which diffuses with an ellipsoidal shape as seen on the xy-plane. This is in agreement with the experimental results by Rausenberger et al. [19,20] on the same reaction.

The non-uniformities, in the form of blocking sites or inert defects changes the oscillatory periods. The effect of increasing continuously their number is to change the period. Besides, we have shown that the interaction between interaction fronts desynchronize the oscillatory behaviour and the system becomes chaotic. If the defects are enough apart, the propagating fronts die before they collide and the oscillatory behaviour is maintained.

Even if we have considered only diffusion of two species, NO and H, these treatment shows the formation of a chemical wave, propagation and death of the perturbation. Considering diffusion of the whole set of species, NO, H, N, O, NH, NH_3 is only more complicated because computational limitations.

Our calculations have shown that even a small fraction of inert defects, around 5%, is enough to change the kinetics of the reaction, changing it from oscillatory to stationary. There is theoretical evidence, mainly by Monte Carlo simulations, that even a small fraction of impurities can make to change the catalytic reaction in related reactions as CO oxidation on Pt(1 0 0) [22]. Finally, let us comment that the propagation of concentration fronts in heterogeneous reaction process can also be modelled by Monte Carlo simulations [21–23]. The Monte Carlo simulation technique is a powerful tool for the study of reacting interfaces and is complementary of studies by ODE's.

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