Study of oscillations and pattern formation in the CO + O$_2$ reaction on Pt(1 0 0) surfaces through dynamic Monte Carlo simulation

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Abstract

Oscillations and pattern formation driven by a surface reconstruction are studied for the catalytic oxidation of CO on Pt(1 0 0) single-crystal surfaces through dynamic Monte Carlo simulations at low pressure and relatively high temperatures conditions. Sustained, modulated, irregular and damped oscillations are observed in our analysis as well as the formation of cellular, target, double spiral, spiral wave and turbulent patterns. The effect and the importance of the hex ⇆ 1 × 1 surface phase transition and partial pressure of the reactants in the gas phase on the behavior of the system are discussed.
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1. Introduction

The heterogeneous catalytic CO + O$_2$ reaction on different metals has received a great deal of attention during the past years both from experimental and theoretical points of view, due to its importance in automobiles and industrials gases emission control. In addition to this importance, there is an intrinsic fundamental interest, since this monomer–dimer reaction, i.e. a reaction involving a particle adsorbing on one site and a particle adsorbing and dissociating on two sites, presents nonlinear phenomena like kinetic oscillations and spatiotemporal pattern formation [1–3].

A variety of catalyzed reactions have been found to show oscillatory behavior under nearly real conditions, i.e. poly-crystalline surfaces or supported catalysts at relatively high pressures, see the reviews of references [1–3] and references therein. Under these conditions, reactions are typically non-isothermal and many effects contribute to obscure the delicate interplay between elementary steps leading to complex behavior. Experimental studies of catalytic reactions on single crystals under isothermal conditions at low pressures have provided valuable information that can be used to develop and evaluate theoretical models based on the microscopic properties of the system. However, these studies have been concerned with only a narrow range of catalytic reactions, mainly CO oxidation on Pt and Pd surfaces and NO reduction by several agents (CO, H$_2$ and NH$_3$) on Pt(1 0 0) and Rh(1 1 0) [2]. It is well known that the (1 0 0) and (1 1 0) faces of noble metals undergo a surface reconstruction driven by adsorbed molecules during these reactions, and this phenomenon is an important ingredient in the appearance of the oscillatory behavior [2–4].

Kinetic oscillations and spatiotemporal patterns have particularly been observed for the CO + O$_2$ reaction on the Pt(1 0 0) surface under isothermal, low pressure conditions ($p \sim 10^{-4}$ to 10^{-1} Pa) [2–9]. Moreover, historically this reaction was the first to be studied showing a well-established mechanism of oscillations under such conditions [5]. Also, it is well known that the clean Pt(1 0 0) surface at $T > 400$ K exhibits a reconstructed quasi-hexagonal configuration (hex) of the atoms in the topmost layer, such reconstructed surface can be lifted by the uptake of molecules such as CO, that is, as soon as the CO coverage on the hex surface reaches a critical value, the formation of a 1 × 1 square structure is triggered [2–18]. The reverse transformation, 1 × 1 → hex, takes place when the CO coverage on the 1 × 1 phase drops below another critical value, i.e. by the creation of empty active sites on the 1 × 1 phase [8–18]. This constitutes an adsorbate-induced hex ⇆ 1 × 1 surface phase transition, which, at $T > 430$ K, is directly involved in the

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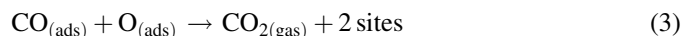E-mail address: giorgio@unsl.edu.ar (G. Zgrablich).

formation of oscillations during the course of the CO + O₂ reaction [2–9,15–18]. The optimum conditions of pressure and temperature to observe temporal and spatial oscillatory behavior for the CO oxidation on the Pt(1 0 0) surface are found to be $pCO \sim 10^{-3}$ Pa, $pO_2 \sim 10^{-2}$ Pa and $460\,K < T < 540\,K$ [4,16].

The appearance of oscillations and spatial structures in the CO + O₂ reaction on Pt(1 0 0) is due to the existence of a coupling mechanism between different parts of the surface, which builds up as a consequence of several elementary processes. The sticking coefficient of oxygen on Pt(1 0 0), S_0, i.e. the probability for an impacting oxygen molecule to stick to the surface, is about 0.1 for the 1×1 phase, whereas it is very small on the hex phase (10^{-3} to 10^{-4}) [2–4,8,10,16,18]. On the other hand, the initial sticking coefficient for CO molecules is almost the same on both phases, that is, $S_0 \approx 0.8$ [8–10,13–16,19]. Therefore, starting with a clean surface in the hex phase, the reaction rate will be initially slow, while the concentration of adsorbed CO increases and, after reaching the critical value, the hex $\rightarrow 1 \times 1$ transformation takes place. For this surface structure, oxygen adsorption–dissociation has a high sticking coefficient, and the adsorbed oxygen atoms react with adjacent CO molecules to form CO₂. Under these conditions the reaction rate is high and sustained by the continuous reaction between adsorbed O atoms and CO molecules arriving either from the gas phase or by diffusion from neighboring sites. Since CO is rapidly reacted and removes by adsorbed O atoms, the coverage of adsorbed CO on the 1×1 phase will now drop below its critical value and the surface transforms into the hex phase and a new cycle starts again [2,4,5,9].

Now, self-sustained oscillations and spatiotemporal patterns are possible only if a coupled or synchronized mechanism is established such that the contributions of different local oscillators do not average out to a stationary reaction rate. In controlled isothermal and low pressure conditions the elementary process leading to this synchronization is the surface diffusion of reactants. A relatively fast surface diffusion of some of the reactants, especially CO, is necessary in order to correlate what is going on in the reaction at relatively distant surface positions [2,8,9,18].

It is now generally accepted that CO oxidation on Pt(1 0 0) proceeds through the so-called Langmuir–Hinshelwood mechanism, which consists of the following sequence of reaction steps [2,5,7–9]:

$$CO_{(gas)} + site \leftrightarrows CO_{(ads)} \tag{1}$$

$$O_{2(gas)} + 2\,sites \rightarrow 2O_{(ads)} \tag{2}$$

$$CO_{(ads)} + O_{(ads)} \rightarrow CO_{2(gas)} + 2\,sites \tag{3}$$

In addition, surface diffusion of adsorbed CO species is also considered.

Theoretical procedures have been implemented to try to explain the experimental behavior of the system. Different kinds of approaches have been mainly used to understand the behavior of CO oxidation on Pt(1 0 0), namely: kinetic equations derived from mean field approximations (MF),

cellular automata (CA) and Monte Carlo (MC) methods [2,3,16,17,20–30]. In the latter case, the behavior of the catalytic system can be simulated in real time units by using dynamic Monte Carlo (DMC) techniques [31].

Gelten et al. [24,25] developed the hexagonal-square (HS) model to try to elucidate the formation of oscillations and spatial patterns in the system. According to their results obtained by DMC simulations, they found that the CO + O₂ reaction on Pt(1 0 0) surface shows different oscillatory regimes as well as a rich variety of spatial structures, namely: cellular, target, double spiral, rotating spirals and turbulent patterns.

The purpose of the present work is to use the HS model in its "on top" version, and a random selection dynamic Monte Carlo method to study in details the influence of the hex $\leftrightarrows 1 \times 1$ surface phase transition and the partial pressure of the reactants in the gas phase on the generation of different oscillatory behaviors, specially modulated oscillations not observed by Gelten et al., and the way these are related to spatio-temporal patterns in a natural way. The manuscript is organized as follows. In Section 2 the model and simulation method are described. Results are presented and discussed in Section 3 highlighting the new behaviors observed in this study. Finally, conclusions are given in Section 4.

2. Model and simulation method

In our analysis we use the HS model in its "on top" version, which is briefly outlined below. The Pt(1 0 0) surface is represented as a regular 2D grid with periodic boundary conditions. The grid consists of $L \times L$ cells; a cell indicates one Pt surface atom, the state of each cell is described by two labels: label 1 identifies the type of molecule or atom that is adsorbed on that cell, it can also represent an empty cell, while label 2 corresponds to the presence of either the hexagonal (H) or the square (S) phases in that cell. In the square phase, each cell has four neighbors and in the hexagonal phase each cell has six neighbors. There are different (label 1:label 2) combinations to indicate the condition of each cell and therefore the processes that can occur on it, for instance: (H:H) indicates an empty cell in the hex phase; (CO:H) an adsorbed CO specie on a cell in the hex phase; (S:S) an empty cell in the 1×1 phase; (X:S) an X (X = CO, O) species adsorbed on a cell in the 1×1 phase. Other details concerning the HS model can be found in references [24,25].

In our model, the time evolution of the system is assumed to occur as a Markovian stochastic process described by a master equation [32,33], which is solved by using a random selection dynamic Monte Carlo method [24,25,34], which, as adapted to our system, is as follows: (i) a surface cell is selected at random with probability $1/N$; where N indicates the total number of cells existing at the moment; (ii) a given i-type reaction step (i.e. adsorption, desorption, diffusion, etc.) is chosen at random with probability W_i/R, where R is the sum of the rates of all possible processes, i.e. the total-transition rate constant of the system; (iii) if the selected i-type reaction step is viable (according to certain rules to be specified below) on the chosen

Table 1
Values of the parameters used in simulations and their comparison with their experimentally observed values

Reaction	p^{exp} (Pa)	p^{sim} (Pa)	S_0^{exp}	S_0^{sim}	References
CO adsorption	$\approx(1-5)\times10^{-3}$	$(1-4)\times10^{-3}$	≈0.8	0.8	[6,10,13,15,19]
O_2 adsorption	$\approx(2-5)\times10^{-2}$	4×10^{-2}	≈0.1	0.1	[6,10,38]
	v^{exp} (s^{-1})	v^{sim} (s^{-1})	E_a^{exp} (kJ/mol)	E_a^{sim} (kJ/mol)	
CO desorption	4×10^{12}–3×10^{15}	1×10^{13}–1×10^{15}	115–159	143.5–159	[11–13,20,35–37]
CO_2 production	2×10^{8}–10^{10}	2×10^{10}	50–100	84	[10,20,35,36]
$1\times1\rightarrow$ hex	2.5×10^{10}–5×10^{11}	1×10^{10}–2×10^{11}	103–107	103–108	[20,35–37]
CO nucleation	–	0.005–0.08	≈0	0	[11–13,15,37]
CO trapping	–	0.005–0.08	≈0	0	[11,15,37]
CO diffusion	–	0–100	–	–	[18,39]

cell, then it is immediately executed; (iv) after a given cell is selected, the time is increased by Δt according to:

$$\Delta t = -\frac{\ln\xi}{NR} \qquad (4)$$

where ξ is a random number selected according to a uniform probability distribution in the interval (0, 1). This equation renders the real time evolution caused by a system transition.

In our simulations we take into account the following elementary processes: CO adsorption, desorption and diffusion, O_2 dissociative adsorption, CO_2 production and surface transformations. The details of these processes can be found in references [24,25]. The corresponding rate constants for each process can be calculated with the parameter values given in Table 1.

3. Results and discussion

In the simulations performed in this work, both the system temperature as well as the partial pressure of O_2 molecules in the gas phase are kept constant, while the partial pressure of CO particles in the gas phase takes different values. Experimentally, CO oxidation on the Pt(1 0 0) crystal face presents kinetic oscillations driven by the hex $\leftrightarrows$ 1×1 surface phase transition in the temperature range $T\approx450$–530 K [2], but more regular temporal behaviors have been observed in the range $T\approx480$–500 K and at partial pressures of CO and O_2 molecules of about 10^{-3} and 10^{-2} Pa, respectively [2–9]. The temperature selected for our analysis was 490 K and the partial pressure of O_2 is 4×10^{-2} Pa, whereas the partial pressures of CO are chosen in the range of $(1-4)\times10^{-3}$ Pa.

The principal results of the CO + O_2 reaction simulation study will be now presented together with a discussion concerning the effect that each reaction step or surface process can produce on the behavior of the system. For the sake of simplicity, the effect of some reaction processes, such as CO diffusion and desorption, temperature and grid size, will not be specifically mentioned throughout this discussion, since these have shown the same behaviors reported by Gelten et al. Therefore, here we concentrate on the effects of the hex $\leftrightarrows$ 1×1 phase transition and of the partial pressure of CO molecules in the gas phase. However, for the sake of

completeness it is important to review the way in which a synchronized mechanism is built up.

3.1. Synchronized mechanism

In our study the appearance of sustained oscillations is possible by means of the development of a synchronized hex $\leftrightarrows$ 1×1 phase transition mechanism. Moreover, sustained oscillations are usually associated to the formation of cellular structures. This synchronized mechanism can be explained as follows.

The simulation of the CO + O_2 reaction on the Pt(1 0 0) surface starts from a completely hex-reconstructed clean surface, on which it is feasible to observe only the adsorption of CO molecules. At a certain surface coverage, small nuclei of CO are formed on the surface; according to certain probability values these clusters can then transform small surface regions from the hex to the square phase thus forming 1×1-CO islands. Afterward, these nuclei can grow by trapping reactions; this part of the evolution of the system is known as the transformation stage. The growth of these islands is a stable process, since the reaction can be locally inhibited by a relatively high adsorbate coverage, which prevents the adsorption and dissociation of O_2. However, when two nn CO molecules desorb from the square phase, or if two nn empty cells are generated on the 1×1 phase by the diffusion of two CO molecules from the square phase toward the hexagonal phase (the diffusion processes can occur across the interface), or alternatively if such cells are created by the diffusion of a CO molecule from the 1×1 phase toward the hex phase and another nn CO molecule desorbs from the same phase, then a O_2 molecule has the possibility of adsorbing and dissociating onto two oxygen atoms. Now, it is pertinent to recall that the 1×1 phase is the one that is active for dissociative O_2 adsorption, while the hex phase is not. If this dissociative adsorption step is accomplished, an adsorbed oxygen atom can then react with an adsorbed CO molecule. Immediately, the formed specie on the 1×1 surface phase desorbs in the form of molecular CO_2 into the gas phase. Thus, new vacant cells appear on the 1×1 phase, since the dissociative O_2 adsorption rate is larger that the CO adsorption rate (note that $pO_2\approx10\,pCO$), then the cells will be preferentially occupied
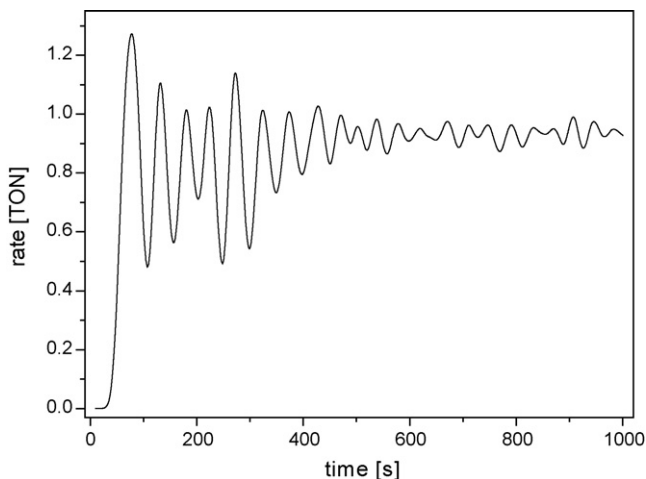
Fig. 1. Damped oscillations during a simulation on a grid of 1024×1024 cells for $pCO = 2 \times 10^{-3}$ Pa. $W_{COdes} \approx 1 \times 10^{-2}$ s^{-1}; $W_{COdif} = 30$ s^{-1}; $W_{H \to S} = 0.075$ s^{-1}; $W_{S \to H} \approx 0.07$ s^{-1}.

by oxygen atoms; subsequently, such atoms can continue reacting with the adsorbed CO molecules. In this way, a reaction front starts to propagate across the surface. As a result of this process, a *reactive stage* is developed on the 1×1 phase. As vacant cells existing on the square phase have a finite probability of undergoing the $1 \times 1 \to$ hex reconstruction, then

small areas of the surface can slowly return to the hexagonal configuration. This last process is known as the *recovery stage*, in this way the reactive stage is gradually extinguished. Since O_2 cannot adsorb and dissociate on the hexagonal phase, CO nuclei will be formed once more and the oscillation cycle will start again with the transformation stage. This synchronized mechanism obtained by simulations is similar to that observed in experiments [2,4,8,9,18]. Local oscillations do not average out due to that fact that the different parts of the surface are coupled through CO diffusion during the formation of sustained oscillations. These oscillations are associated with the formation of cellular patterns, which have been observed experimentally [39,40].

3.2. Effect of the surface transformation

The model employed here is very sensitive to the hex $\to 1 \times 1$ phase transition. Sustained oscillations can be observed if nucleation and trapping rates have frequency values between 0.015 and 0.03 s^{-1}. If these values are increased, the sustained oscillations decay toward damped oscillations, because the transformation stage becomes faster than the recovery stage. In fact, an empty cell undergoing a $1 \times 1 \to$ hex phase transition can be occupied by a CO molecule and quickly reconstructs toward the square phase by
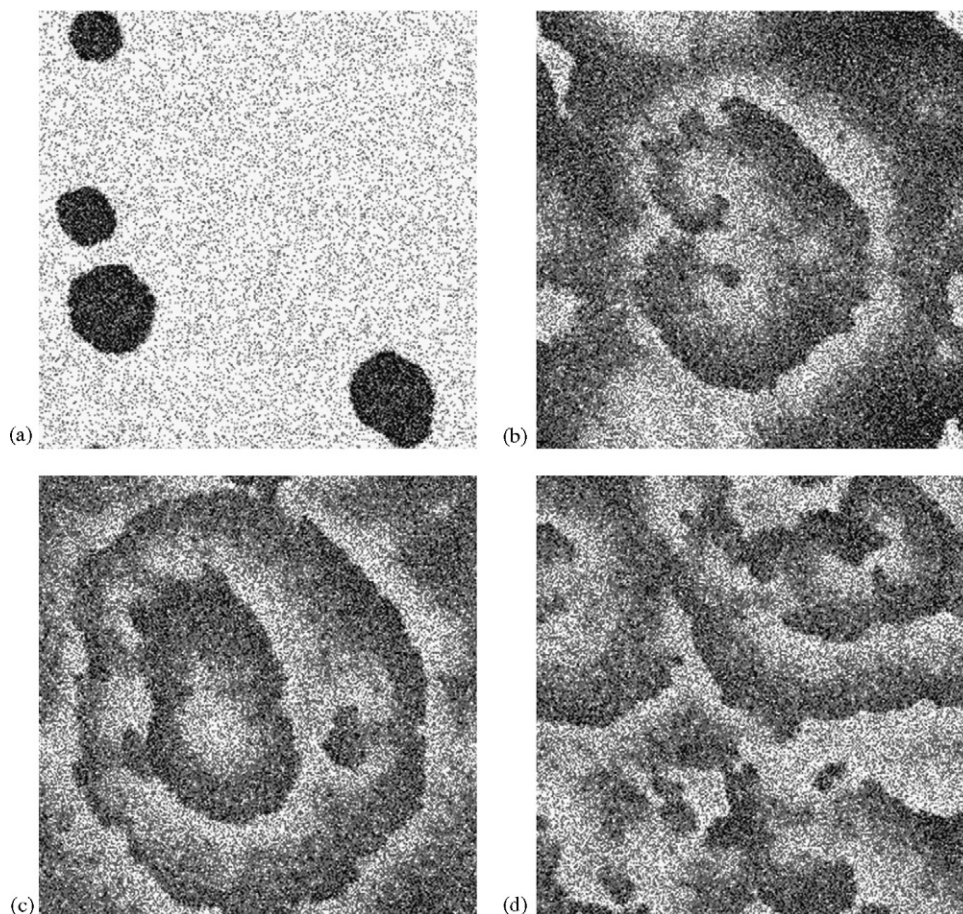

Fig. 2. Different kinds of spatial patterns: (a) 40 s; (b) 370 s; (c) 430 s; (d) 600 s. Grey areas indicate adsorbed CO on the hex phase and empty cells on hex and 1×1 phases, white areas show adsorbed CO on the 1×1 phase and black areas correspond to the adsorbed oxygen.

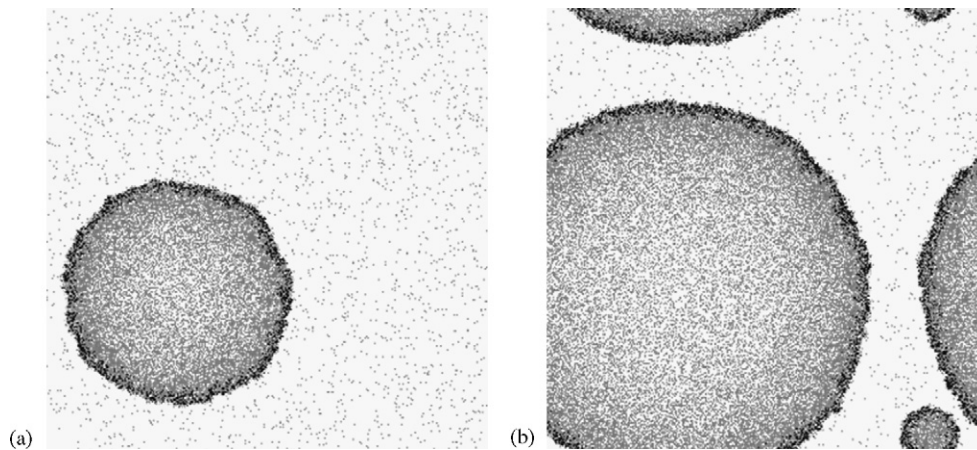Fig. 3. Snapshots showing the formation of cellular structures: (a) 80 s and (b) 100 s. $W_{COdes} \approx 1 \times 10^{-3}$ s^{-1}; $W_{COdif} = 30$ s^{-1}; $W_{H \rightarrow S} = 0.03$ s^{-1}; $W_{S \rightarrow H} \approx 1.0$ s^{-1}. The color of the areas is the same as in Fig. 2.

means of trapping or nucleation reactions. Such molecules can desorb from the square phase and, if O$_2$ adsorbs and dissociates, a new reaction front is formed, while the old reaction fronts are not completely extinguished. This destroys the synchronized mechanism. The oscillatory behavior obtained by this effect is shown in Fig. 1. This behavior is accompanied by different spatial patterns, which are generated one after another, presented in Fig. 2: (a) cellular, (b) double spiral, (c) target and (d) turbulent. When the nucleation and trapping rates are

decreased, the oscillation period is longer, since the slowing down of these processes delays the transformation stage.

On the other hand, when the $1 \times 1 \rightarrow$ hex transformation rate attains values in the range of about 0.05–1.5 s^{-1}, sustained oscillations are observed. If this transformation rate is increased within this range, i.e. it is increased from 0.05 to 1.5 s^{-1}, the reaction fronts become thinner; this is due to the fact that the recuperation stage is faster, the empty cells created by the reaction between CO and O have more probability to return to
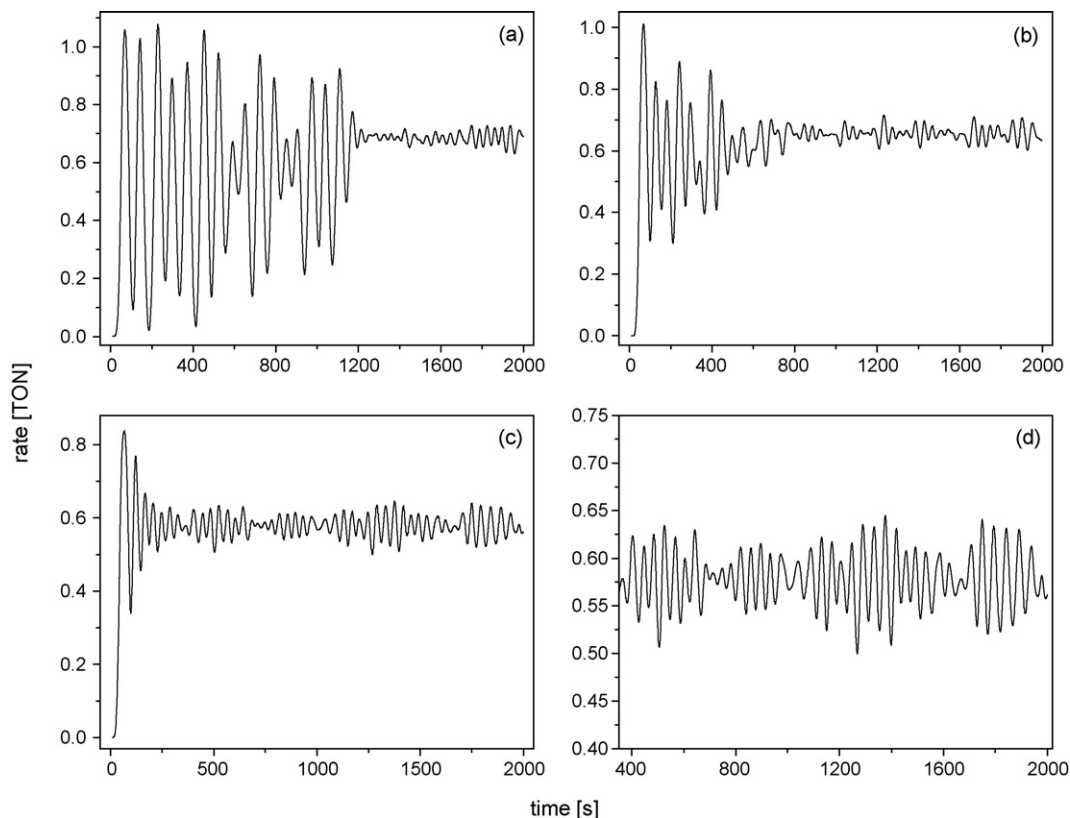

Fig. 4. Damped oscillations: (a) $pCO = 1.5 \times 10^{-3}$ Pa; (b) $pCO = 1.3 \times 10^{-3}$ Pa. Modulated oscillations: (c) $pCO = 1 \times 10^{-3}$ Pa; (d) Fig. 4(c) enlarged. $W_{COdes} \approx 1 \times 10^{-2}$ s^{-1}; $W_{COdif} = 30$ s^{-1}; $W_{H \rightarrow S} = 0.015$ s^{-1}; $W_{S \rightarrow H} \approx 0.07$ s^{-1}.

the hex phase. Fig. 3 shows this spatial behavior for a grid with 1024×1024 cells for $p\mathrm{CO} = 2 \times 10^{-3}$ Pa. When the $1 \times 1 \rightarrow$ hex restructuring rate is higher than $1.5\ \mathrm{s}^{-1}$ the sustained oscillations disappear and the spatial patterns are destroyed. As it can be observed in Fig. 3, the amount of oxygen atoms decreases on the 1×1 phase, while the amount of adsorbed CO molecules increases on the surface, therefore if this process rate increases even more, then the CO species will be in excess and there are no enough O atoms to react with them, which leads to the surface poisoning by CO molecules on the square phase. The contrary case is observed if the value of the restructuring rate is lower than $0.05\ \mathrm{s}^{-1}$: oxygen atoms are in excess and there are few adsorbed CO molecules on the surface, in this way the 1×1 phase does not have enough strength to progress, then destroying the synchronized mechanism.

3.3. Influence of pCO

As one of the principal factors, we have studied the effect of the partial pressure of CO molecules in the gas phase on the system. In our simulations we have observed that if $p\mathrm{CO}$ is higher than 2×10^{-3} Pa the sustained oscillation period is longer. This phenomenon can be explained as follows: if $p\mathrm{CO}$ in the gas phase increases, the adsorption probability of CO

molecules also increases, then the probability of finding two nn empty cells remain on the 1×1 phase decreases, since an empty cell on the 1×1 phase has a higher probability of being occupied by a CO molecule, therefore the process of adsorption and dissociation of oxygen molecules and the formation of some reaction front is delayed. On the contrary, when $p\mathrm{CO}$ is lower than 2×10^{-3} Pa, the oscillation period is shorter. But, if this partial pressure decreases even more, sustained oscillations decline in favor of damped and modulated oscillations. This is so because if the $p\mathrm{CO}$ decreases, then the creation of empty pairs of nn cells on the 1×1 phase is favored and many reaction fronts are generated and the synchronized mechanism is destroyed. Fig. 4 shows the effect of the partial pressure of CO molecules on the oscillatory behavior for grid sizes of 1024×1024 cells.

In this work we have obtained an interesting new feature for CO oxidation represented by modulated oscillations, as it can be seen in Fig. 4(c) and (d). Our experience in other systems, in particular in the NO + CO reaction on the Pt(1 0 0) surface [41,42], indicates that the manifestation of this oscillatory behavior could be due to a competing effect between the dissociation rate of the molecule to dissociate, in that case NO, and the production rate of the molecules formed, in that case N_2 and CO_2. In the present study, we believe that this interesting phenomenon is due to similar circumstances. In this case, as
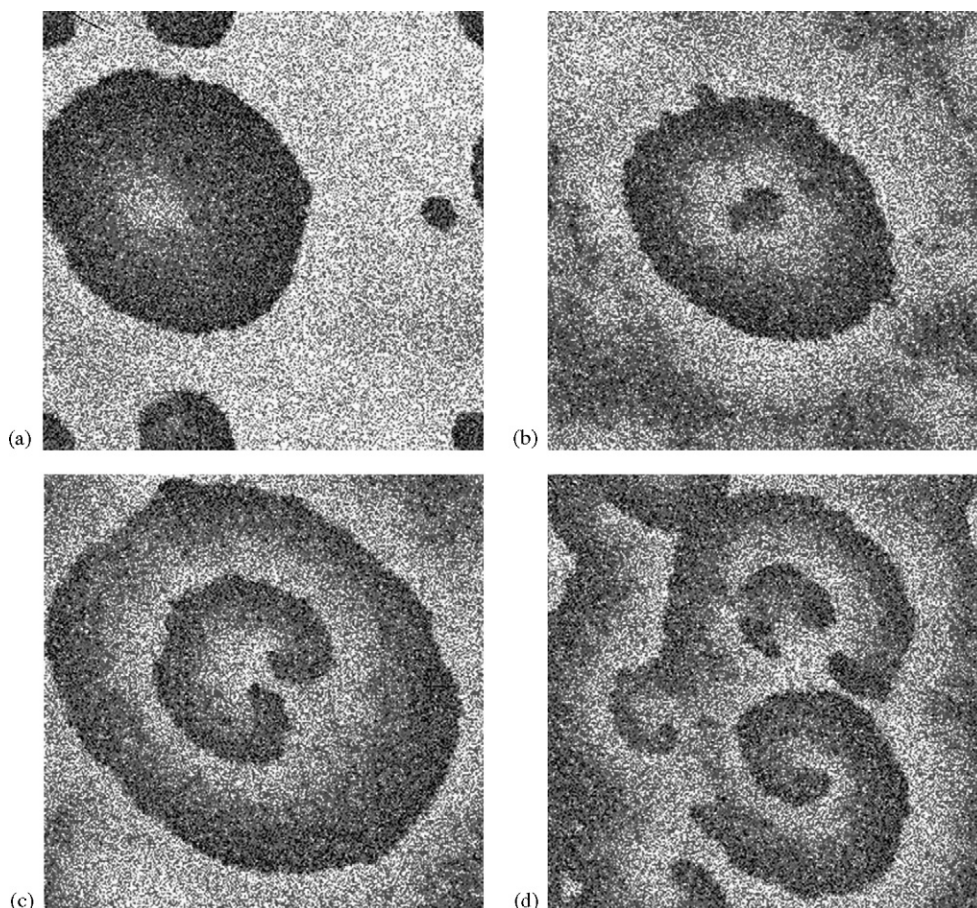

Fig. 5. Snapshots showing the formation of different kinds of spatiotemporal patterns during the oscillations of Fig. 4(a): (a) 770 s; (b) 1130 s; (c) 1195 s; (d) 1780 s. The color of the areas is the same as in Fig. 2.

pCO decreases, oxygen molecules have more probability to adsorb and dissociate, therefore the amount of adsorbed CO molecules is not enough to consume the adsorbed O atoms and establish a regular oscillatory regime, but it is enough to form a pulsed regime.

Oscillations of Fig. 4(a) merit a good deal of attention, given that such oscillations are accompanied by a rich diversity of spatial patterns, which are illustrated in Fig. 5. When the simulation starts, irregular oscillations are observed, which show the formation of cellular patterns (Fig. 5(a)), when some time is elapsed in the reaction the oscillation is attenuated toward a damped regime, whereas on the surface the cellular structure declines in target (Fig. 5(b)), double spiral (Fig. 5(c)), spiral wave (Fig. 5(d)) and turbulent (this snapshot is not shown here) patterns. Fig. 5(d) is in concordance with the experimental evidences, since this kind of "spiral wave" have been observed in the CO + O₂ reaction on Pt(1 0 0) surface [18]. This same pattern also have been observed during the NO + CO reaction on Pt(1 0 0) surface [43]. The formation of target patterns have been experimentally observed in the CO + O₂ reaction on Pt(1 1 0) surface [39,40].

In the simulations these different patterns appears in the CO + O₂ reaction on Pt(1 0 0) because, when a cellular structure has grown sufficiently in size, then there is the possibility that in the inside of the first reaction front a second structure can form and grow up, causing the formation of a target pattern. As was mentioned, when pCO decreases the empty cells increase on the 1×1 phase, therefore they are preferentially occupied by oxygen atoms and have also more opportunity to return back to the hex phase. In this later case, the hex phase grows in the inside edge of the first front and, as these cells can only be occupied by CO, and as the reaction between CO molecules and O atoms can take place across phase boundaries, then the structure of the second front can undergo a breaking in an small portion of the edge, which causes that a double spiral starts to generate on the surface. At the beginnings this pattern is not clearly distinguished, but, as time passes, the double spiral is entirely formed, as it can be observed in Fig. 5(c). Due to the fact that the double spiral structure is symmetrical, the two branches collide between them creating a cellular pattern, but remnant material (oxygen atoms) of the branches stay in the inside of the cellular pattern forming a new double spiral. Such spirals are stable during a long time; however, when enough time has passed they are transformed in a spiral wave. Afterward the spiral wave declines into a turbulent regime, which is indefinitely maintained.

4. Conclusions

We have studied by dynamic Monte Carlo simulations the oscillatory behavior of the CO + O₂ reaction on Pt(1 0 0) in the high temperature and low pressure range. This study is partially based in the HS model, which was originally used by Gelten et al. [24,25]. It is pertinent to mention that Gelten et al. also reported some temporal and spatiotemporal phenomena observed in this study. However, they observed that the spatial

patterns (target and double spiral) are obtained when the CO adsorption rate is increased beyond a certain value. Whereas, we have obtained these structures through two ways: (1) when the CO nucleation and trapping rates are increases beyond a given value, and (2) when pCO is decreased below a certain value. Moreover, Gelten et al. did not observe modulated oscillations, therefore the present analysis discloses a new oscillatory behavior in the system.

A first general result of the present study is the appearance of a sustained oscillatory behavior associated with the formation of cellular patterns. In this work we only mention the effect of the rate of the phase transformations and the behavior of the oscillation under changes in the partial pressure of CO, which have been investigated in detail with the following principal results:

(a) Sustained oscillations can only be observed if a synchronized mechanism is achieved and also if cellular spatial patterns are formed. On the other hand, when irregular, modulated and damped oscillations are observed, the synchronization is always removed and cellular structures can decay in target, double spiral, spiral wave and turbulent spatial behaviors. This latter structure is maintained indefinitely. Experimentally, the oscillatory behavior is associated with spatial pattern formation in a similar way [2].

(b) Sustained oscillations are obtained when nucleation and trapping rates have values between 0.015 and 0.03 s⁻¹. If these values are increased, the sustained oscillations are transformed in damped oscillations. This oscillatory behavior is accompanied by different spatial structures: cellular, target, double spiral and turbulent patterns. If the nucleation and trapping rates are decreased, the sustained oscillation period is longer.

On the other hand, sustained oscillations are observed if the $1 \times 1 \rightarrow$ hex transformation rate has values in the range of about 0.05–1.5 s⁻¹.

(c) Sustained oscillations are observed when pCO = 2 × 10⁻³ Pa. If such value is increased the sustained oscillation periods become longer. However, when pCO is decreased the oscillatory behavior decline in favor of damped and modulated regimes. This interesting phenomenon is observed due to an increase in the effective dissociative adsorption rate of O₂. When damped oscillations are formed in the system, they can be accompanied by sequential spatial patterns: cellular, target, double spiral, spiral wave and turbulent. This later structure is maintained indefinitely thereafter.

In summary, this study reveals many features observed experimentally in catalytic reactions on the Pt(1 0 0) crystal, or inclusive on other single crystal surfaces.

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