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Journal of Molecular Catalysis A: Chemical 167 (2001) 121–128

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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# Toward the study of catalytic reactions under industrial conditions: a contaminated CO oxidation model

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Received 1 May 2000

**Abstract**

Recent trends in surface chemistry are trying to bridge the gap between ideal ultrahigh vacuum (UHV) studies and results of catalytic reactions under industrial conditions. These conditions are mainly characterized by a heterogeneous active phase, high pressure and the presence of contaminant species. In the present work we address the last of these three factors. More precisely we study the effects of a contaminating species, whose only action is adsorption and desorption being otherwise inert, on the kinetics of CO oxidation on transition metals. We introduce a suitably modified Ziff–Gulari–Barshad model, a contaminated ZGB model, and obtain by Monte Carlo simulations the behavior of the steady state of the system for different CO and contaminant concentrations. We find that the reaction window shrinks with increasing contaminant concentration until it disappears at a critical value. Moreover, we find that the classical lower bound ZGB irreversible phase transition is unaffected while the upper bound first order transition transforms continuously into a second order one with increasing contaminant concentration, as revealed by the behavior of critical exponents. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Contaminant species; ZGB model; Monte Carlo simulations

## 1. Introduction

Catalytic reactions performed under industrial conditions are usually very far apart from studies of molecular reactions on ideal systems in ultrahigh vacuum (UHV) and sometimes it is difficult to extrapolate results and conclusions from one region to the other. Industrial conditions are mainly characterized by three factors: (a) the active solid is not a perfect crystal but rather a heterogeneous active phase; (b) the reaction does not occur in UHV but at a pressure many orders of magnitude higher under thermodynamic equilibrium between the gas phase and the adsorbed phase; (c) the reactants are not pure but contaminated with other species.

Recent researches in surface science [1–6] are opening a new trend in the research of catalytic reactions, in the sense that they try to bridge the gap between ideal ultrahigh vacuum (UHV) studies of molecular reactions on perfect crystals and the results of catalytic reactions performed in industrial conditions [7]. Some of the recent developments allow atomic scale monitoring of surface species during catalytic reactions at high pressures both on flat and stepped crystals [1–3], while others deal with adsorption and reaction kinetics studies at high pressure on different surfaces [4–6]. All these studies are revealing novel behaviors not observed in UHV studies.

In the present work we address from a theoretical point of view the effects of the third factor mentioned

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PII: S1381-1169(00)00499-4

above, the presence of a contaminating species, on a widely studied reaction: the monomer–dimer (MD) irreversible reaction, inspired in the catalytic oxidation of CO, which presents many interesting features and, in particular, shows kinetic phase transitions, a problem of actual theoretical interest.

## 2. Model and simulation method

The study of kinetic, or irreversible, phase transitions (IPT) exploded since the seminal work of Ziff, Gulari and Barshad [8], who proposed the popular ZGB model, and has continued attracting the attention of researchers ever since [9,10]. Even if the ZGB model is oversimplified, it has proven to be useful in the understanding of some of the principal characteristics, of some complexity, of the kinetics of CO oxidation.

The outstanding feature of this model is to present a reaction window delimited by an oxygen-poisoned state characterized by a second order IPT, at low CO concentration, and by a CO-poisoned state characterized by a first order IPT, at high CO concentration. This behavior is a consequence of a delicate site-particles stoichiometric balance: $O_2$, as a dimer, needs two empty nearest neighbor sites for dissociative chemisorption, while CO, as a monomer, needs only one. Such condition induces spatial correlations leading to poisoned steady states under the appropriate conditions.

For this reason we propose here a contaminated ZGB model in which the contaminant action disturbs, in a reversible way, the availability of adsorption sites. Even though we have in mind the CO oxidation reaction, we formulate our model in a general way to study the effects of a monomer contaminant species on a general MD reaction.

Let A be the monomer, $B_2$ the dimer and C the contaminant. We propose the following reaction steps:

$$\mathrm{A\,(gas)} + \mathrm{site} \rightarrow \mathrm{A\,(ads)} \tag{1}$$

$$\mathrm{B_2\,(gas)} + 2\,\mathrm{sites} \rightarrow 2\mathrm{B\,(ads)} \tag{2}$$

$$\mathrm{C\,(gas)} + \mathrm{site} \leftrightarrow \mathrm{C\,(ads)} \tag{3}$$

$$\mathrm{A\,(ads)} + \mathrm{B\,(ads)} \rightarrow \mathrm{AB\,(gas)} + 2\,\mathrm{sites} \tag{4}$$

In the CO oxidation reaction, for example, A is CO, $B_2$ is $O_2$, AB is $CO_2$ and C could be any impurity in the reactant gases, for example, $N_2$. In the above reaction system the contaminant species C only undergoes adsorption–desorption processes, being otherwise inert. As we shall see, even very small amounts of contaminant, as those present in realistic reaction conditions, affect drastically the reaction kinetics and the position and characteristics of the IPTs.

We study the behavior of the proposed system through Monte Carlo simulation by following closely the method used in the original ZGB model [8], with the obvious modifications imposed by step (3). The catalyst surface is represented by a square lattice of sites, with dimensions $L \times L$ ($L = 100$ in our simulations) and periodic boundary conditions. The gas phase is represented by a mixture of the three reactant species with mole fractions $Y_A$, $Y_B$ and $Y_C$, such that they sum up to unity.

A trial begins by choosing a species from the gas phase with probabilities given by the respective mole fractions. If the chosen molecule is A, then: (a) a site on the lattice is chosen at random; (b) if that site is already occupied, then the trial ends; (c) otherwise A is adsorbed; (d) the four nearest neighbors (NN) sites are checked in random order, if B is found in any of them, then both sites are emptied and a reaction product AB is accumulated. If the chosen molecule is $B_2$, then: (a) two adjacent sites are chosen at random; (b) if either site is occupied, the trial ends; (c) otherwise $B_2$ dissociates and adsorbs on those two sites; (d) the six NN sites are checked in random order, if an A is found in any of them, then it is reacted with the adjacent B, both sites are emptied and a reaction product AB is accumulated. If the chosen molecule is C, then: (a) a site on the lattice is chosen at random; (b) if it is occupied, then the trial ends; (c) otherwise C is adsorbed; (d) another site in the lattice is randomly chosen; ( e) if it is C, then it is desorbed, otherwise the trial ends. [1]

A Monte Carlo step (MCS) consists of $L \times L$ trials, i.e. in the mean every site on the lattice has

[1] This particular kinetics for the adsorption–desorption process for C is one of the many that could have been chosen. This kinetics, if C were the only species present in the system, would lead to complete saturation of the surface. The effects of assuming different kinetics will be discussed elsewhere.

been visited for adsorption. For given values of $Y_A$ and $Y_C$, and starting with an initial blank state, stabilization of the process is achieved either when the total surface coverage $\theta = \theta_A + \theta_B + \theta_C$ is unity or when it has not changed appreciably over the last $10^5$ MCS. In all cases stabilization is achieved before $70 \times 10^5$ MCS. In this way a plot of each species coverage and of the reaction rate $R_{AB}$ versus $Y_A$ is obtained for each value of $Y_C$.

## 3. Results and discussion

As shown in Fig. 1, the behavior of the steady state coverage and that of the reaction rate as a function of $Y_A$ is strongly affected by the contaminant concentration. In (a) for $Y_C = 0$, we have the classical ZGB behavior with a second order IPT at $Y_{1A} = 0.389 \pm 0.005$ (for $Y_A < Y_{1A}$ there is a B-poisoned state) and a first order one at $Y_{2A} = 0.525 \pm 0.001$ (for $Y_A > Y_{2A}$ there is an A-poisoned state) and the reaction window between these two values. As $Y_C$ increases (b) and (c) the low $Y_A$ IPT remains unchanged, with the only exception that near $Y_{1A}$ few C particles also contribute to the B-poisoned state, while the high $Y_A$ IPT becomes smoother and continuously moves to the left until the reaction window completely disappears (d) when the contaminant concentration reaches a critical value $Y_C^{crit} \approx 7.5 \times 10^{-7}$ for the assumed kinetics. The behavior of the reaction window can be better appreciated in Fig. 2, where only the total surface coverage has been represented as a function of $Y_A$. The bounds of the reaction window (broken lines) have now been marked as $Y_{B+C}$ and $Y_{A+C}$ in order to stress the fact that the two poisoned states include the contaminant species, a few molecules in the lower bound and an appreciable fraction in the higher one. [2]

In order to analyze these results we must recall that, as it is well known from the ZGB model, the A-poisoned state is achieved through an abrupt growing of A-islands when criticality is approached. When $Y_A$ is not sufficiently high, adsorption of the dimer $B_2$ and the eventual reaction prevents the explosive growth of islands and the reaction is sustained. Let us see what happens near $Y_{A+C}$ (for example, $Y_A = 0.47$ in Figs. 1 and 2(b), corresponding to $Y_C/Y_C^{crit} = 0.13$) when the contaminant C is present. At an intermediate stage in the stabilization process, where $\theta_A = 0.0348$, $\theta_B = 0.5380$ and $\theta_C = 0.0896$ (snapshots not shown), the contaminant in the adsorbed phase is in part dispersed among a sea of Bs and empty sites while another fraction is in contact with small A-islands. The former have negligible effect on the process since the adsorption of the monomer A on empty sites next to Bs is still highly probable. On the contrary, those Cs in contact with small A-islands prevent partially the breaking down of these by the adsorption of the dimer, through a decrease in the adsorption probability of a dimer in their surroundings (two sites are needed). In a sense, we could say that C favors the nucleation and growth of these islands. As the process goes on, at a stage where $\theta_A = 0.2668$, $\theta_B = 0.2508$ and $\theta_C = 0.1492$, A-islands are much bigger, with an appreciable amount of Cs trapped inside and another fraction in contact with their borders, while the situation in the sea of Bs and empty sites is similar to that corresponding to the previous stage. All this results in a multiple island nucleation, growth and coalescence process leading continuously to the A-poisoned state, with some Cs imbedded inside, ending up with coverages given by $\theta_A = 0.8424$, $\theta_B = 0$ and $\theta_C = 0.1576$. The overall effect of the contaminant is then to make the reaction process near the upper bound to appear as that corresponding to a higher effective A concentration. This explains why the reaction window shrinks, by shifting the upper bound to the left while the lower bound remains unaffected.

The form in which the reaction window, $\Delta Y_A$, shrinks as a function of $Y_C$ is represented in Fig. 3. In the neighborhood of $Y_C^{crit}$, where the window disappears, $\Delta Y_A$ behaves as $\Delta Y_A \propto (Y_C^{crit} - Y_C)^{\zeta}$ with $\zeta = 2.83 \pm 0.23$, giving a critical value of $Y_C^{crit} = (7.5 \pm 0.2) \times 10^{-7}$. Fig. 4 shows the phase diagram for the reaction considered, with the B-poisoned, the (B + C)-poisoned (in the inset), the reactive, the (A + C)-poisoned and the A-poisoned zones.

Finally, we investigated the nature of the phase transitions at the lower and upper bounds delimiting the reaction window. In order to avoid the large fluctuations problems arising near criticality [9,10], we made use of the epidemic analysis due to Jensen et al. [11] and the method of Evans and Miesch [12,13] to obtain critical exponents. At the lower bound, we start with a

[2] In some cases the upper bound poisoned state may also contain some few Bs completely surrounded by Cs.

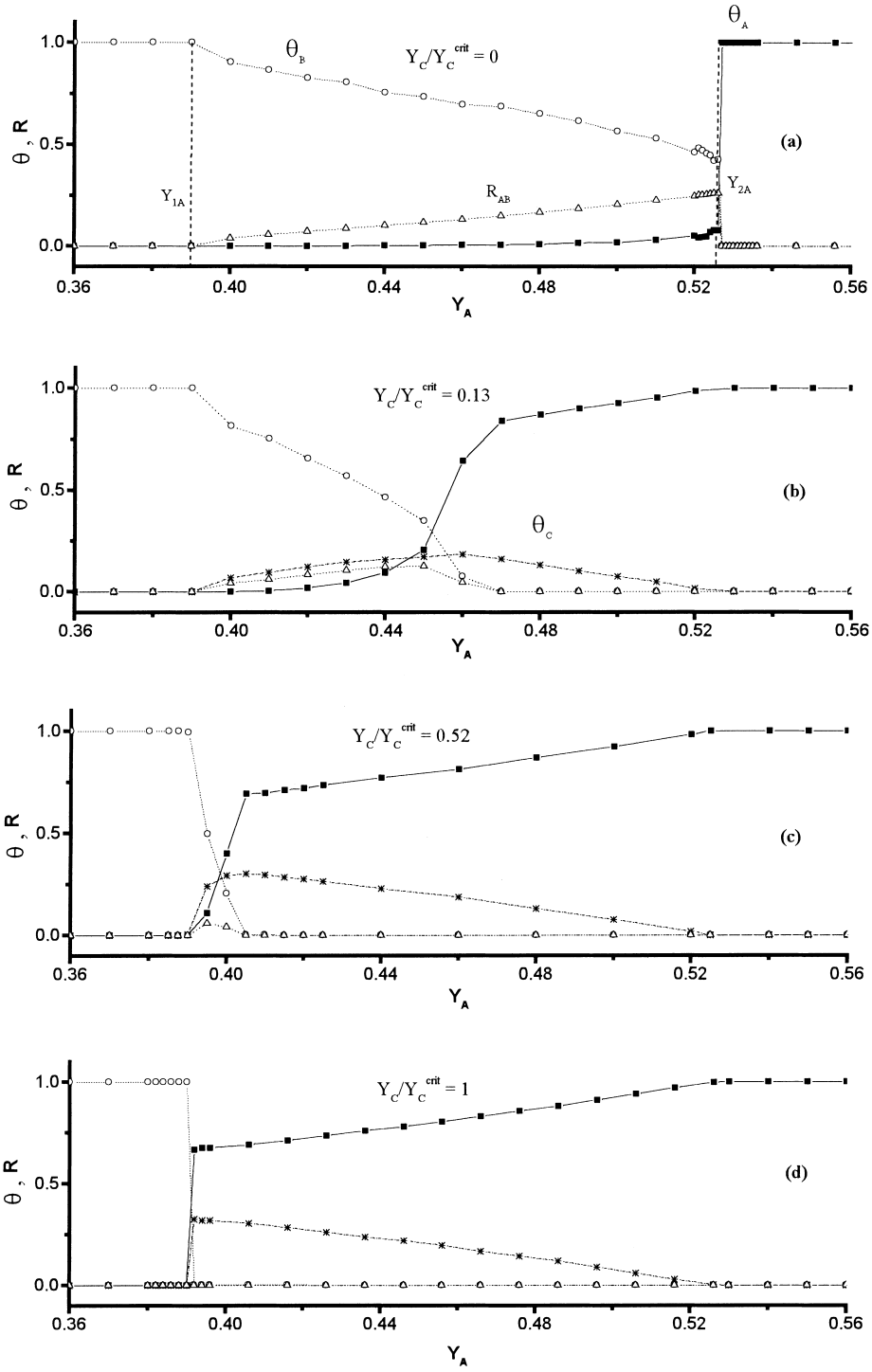


Fig. 1. Steady state mean coverages and reaction rate for the contaminated monomer–dimer reaction, for different contaminant concentrations increasing from (a) to (c).

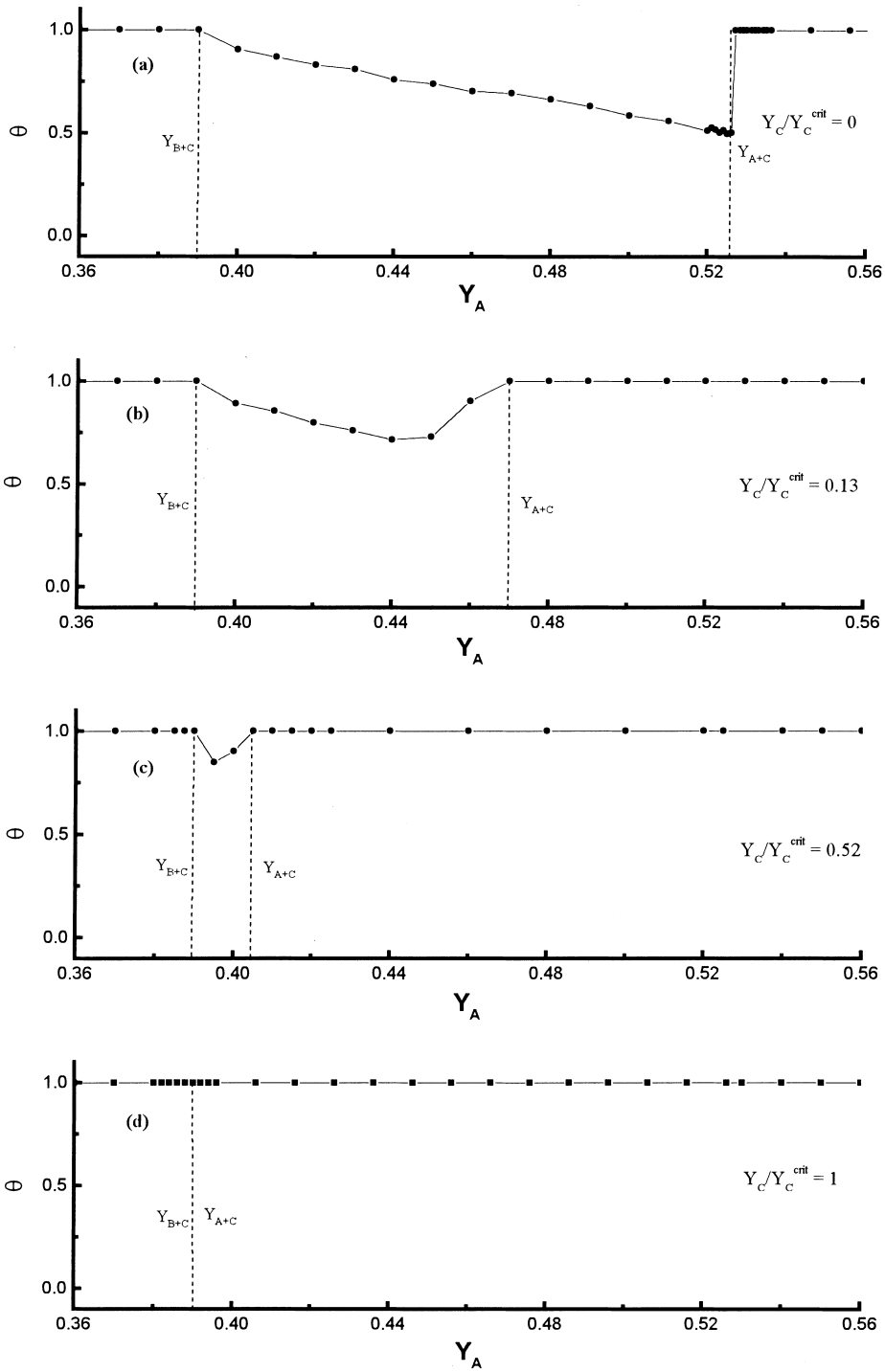


Fig. 2. Steady state total mean coverage showing the shrinking of the reaction window as the contaminant concentration increases from (a) to (c).

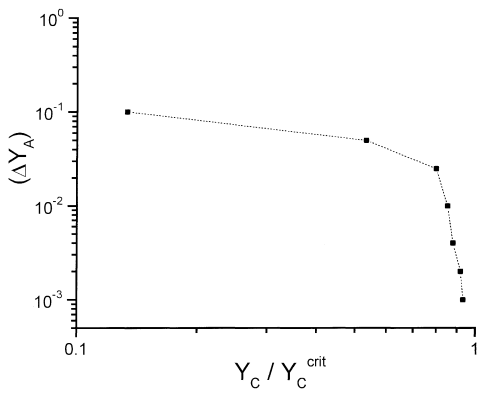


Fig. 3. Variation of the size of the reaction window as a function of the contaminant concentration.

lattice completely covered with B-species except for a single empty sites at its center. Then we measure the survival probability $P(t)$, i.e. the probability that the lattice is not completely poisoned after time $t$, and the average number of empty sites $N(t)$. These quantities should scale as:

$$P(t) \propto t^{-\delta} \tag{5}$$

$$N(t) \propto t^{\eta} \tag{6}$$

A unit of time is represented by one MCS following the trial procedure described above and for each time the measured quantities were averaged over $5 \times 10^3$ realizations of the process. Results for the critical exponents $\delta$ and $\eta$ are shown in Fig. 5(a) for different

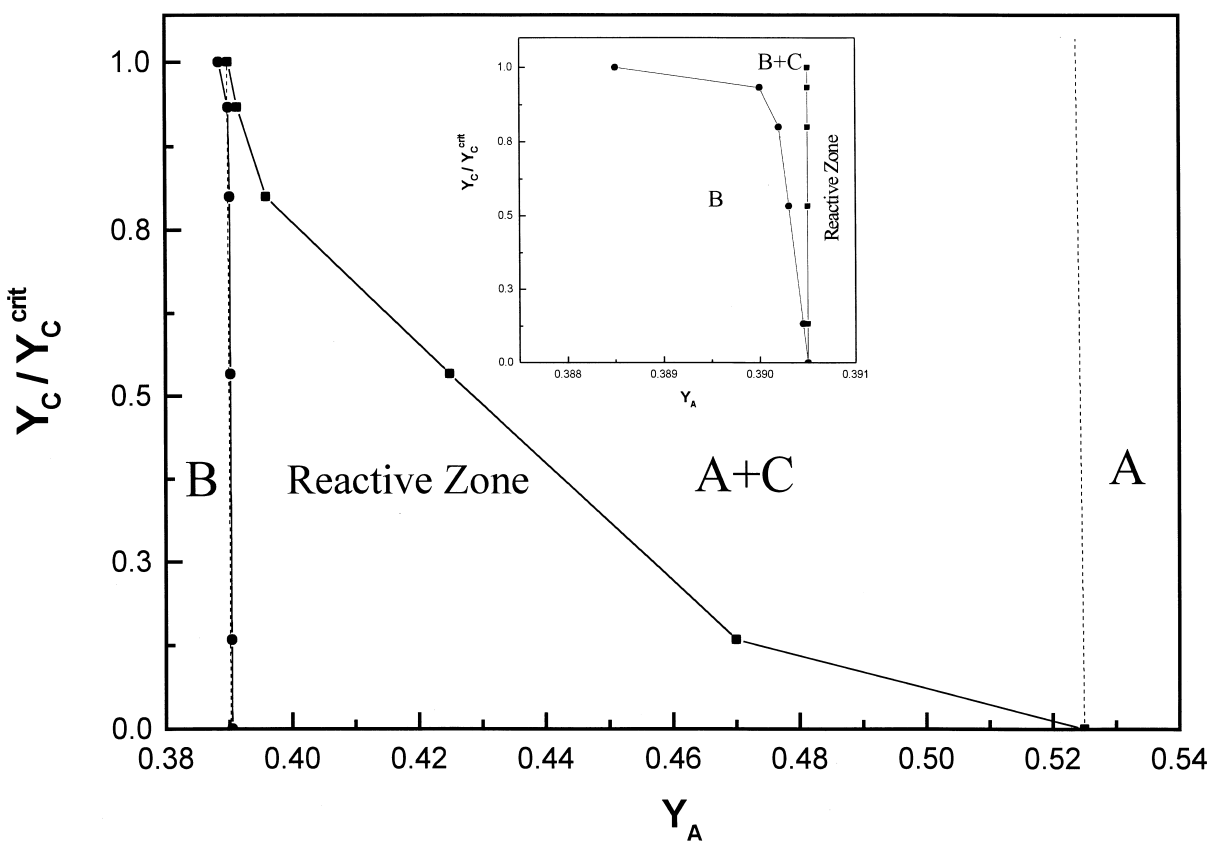


Fig. 4. Phase diagram for the contaminated monomer–dimer reaction showing the different poisoned regions and the reaction region. The inset shows an enlargement near the lower bound of the reaction window.

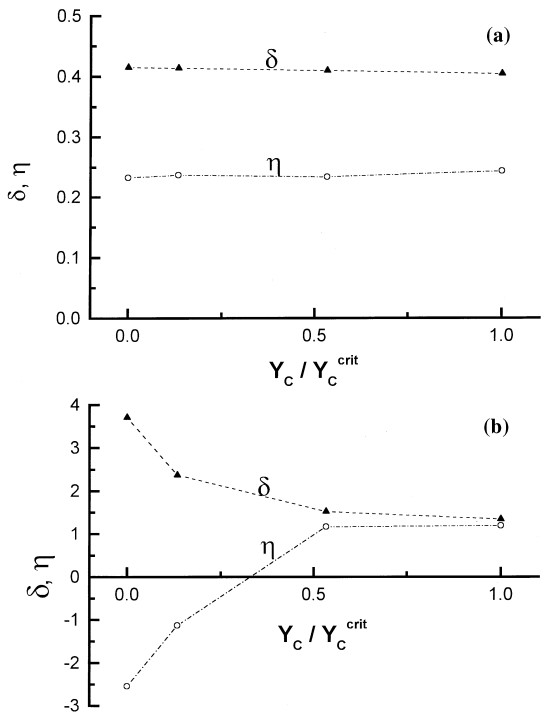


Fig. 5. Critical exponents $\delta$ and $\eta$ as a function of the contaminant concentration: (a) at the lower bound of the reaction window the IPT is second order and the exponents are constant; (b) at the upper bound the IPT is first order at low contaminant concentration ($\delta > 0$ and $\eta < 0$) and changes to second order ($\delta > 0$ and $\eta > 0$) as the concentration increases.

values of $Y_C$. They appear to be independent of the contaminant concentration, their values are in concordance with the results obtained by Jensen et al. [11] for the pure ZGB model and characterize a second order IPT belonging to the universality class of directed percolation. A similar analysis was performed at the upper bound, except that we start with a pair of nearest neighbor empty sites imbedded in a lattice covered by A-species. Results for the critical exponents as a function of $Y_C$ are shown in Fig. 5(b). Here we find a drastic change in the characteristics of the IPT: for $Y_C = 0$, the pure ZGB model, the results are in concordance with those obtained by Evans and Miesch [12,13] and characterize a first order IPT; as $Y_C$ increases, $\delta$ decreases while $\eta$ increases until the latter changes its sign around $Y_C/Y_C^{crit} \approx 0.26$; finally, by further increasing $Y_C$ the critical exponents appear to converge to the same value. Following the analysis performed in [12,13], we can conclude that this variation of the critical exponents is due to the fact that the presence of the contaminant species affects the reaction rate through the same topological mechanism affecting the growth of A-islands explained above. In particular we find that the IPT at this upper bound has changed from first order (for $Y_C = 0$) to second order (for $Y_C > 0$) however, this second order transition is determined, through the analysis of critical exponents, not to be in the directed percolation universality class. This change in the order of the phase transition is in concordance with our observation that in the contaminated case the monomer poisoned state is reached through a continuous process of nucleation, growth and coalescence of islands, rather than trough an explosive growth of a compact island (condensation) as it happens in the original ZGB model.

## 4. Conclusions

In summary, we have examined the changes in the kinetics of the monomer-dimer catalyzed reaction, like the CO oxidation reaction, represented by the ZGB model, produced by the presence of vestiges of a contaminant species in the gas phase which only undergoes adsorption–desorption processes, being otherwise inert. We have found that the second order IPT at the lower bound of the reaction window is not affected by the contaminant, except that the B-poisoned state may contain a few C molecules, and continues belonging to the directed percolation universality class. On the contrary, the higher bound shifts to lower $Y_A$ values as $Y_C$ increases producing a shrinking of the reaction window, which completely disappears at a critical value $Y_C^{crit}$. Moreover, for $Y_C > 0$ the first order IPT changes its character to a second order IPT not belonging to the directed percolation universality class.

## Acknowledgements

This research was partially supported by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) of Argentina. The authors would also like to thank their colleague V. Pereyra for helpful discussions.

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