



*Dedicated to Professor Bogdan C. Simionescu
on the occasion of his 70th anniversary*

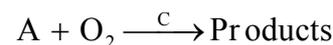
OSCILLATIONS IN THE SYSTEM ADSORBED CARBON/CATALYTIC SURFACE

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Received August 23, 2017

Two models in which carbon atoms are involved in a chemical reaction can be an explanation for the oscillations in heterogeneous catalytic systems in which these carbon atoms are involved. These models are based on the carbon atoms adsorbed on a free surface site or the reversible transformation of a free surface site in a free subsurface site.



INTRODUCTION

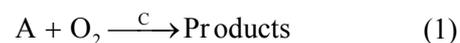
Heterogeneous catalytic reactions are non-linear multilevel chemical reaction systems far from thermodynamic equilibrium which exhibit complex temporal behavior such as instabilities, oscillations, chemical waves or chaos.¹ The oscillations cycles of different products may have different forms and surface phases with respect to each other. These facts can produce valuable information on the kinetics and mechanism of these reactions. This explains also the great number of kinetic and mathematical models for modeling or simulation of the chemical oscillations.²⁻¹¹

If in reaction one reactant is a gaseous hydrocarbon, it can happen that due to pyrolysis or other processes, carbon atoms may be obtained and deposited on the catalysts surface and in its bulk. In this case a slow deactivation of the catalyst occurs which can be a cause of producing chemical oscillations.^{12,13,14}

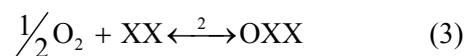
The goal of this paper is to see if the presence of the deposited carbon on free catalytic surface sites and oxygen from the gas phase or from the surface could produce oscillatory reactions.

THE MODEL

Let the reaction be:



In case of the carbon presence on the catalyst surface this equation can be described by the following steps:

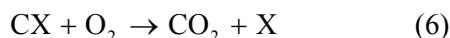


In equations (1)-(5) A and O₂ are gaseous reactants, C the carbon impurity, X the free site of the surface, AX and OXX the reactive adsorbed species of A and oxygen and CX the adsorbed species of carbon. This last species is involved in the buffer step of the system.

When one of the reactants is a gaseous hydrocarbon, due to the pyrolysis or oxidative pyrolysis processes, carbon may be obtained and

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deposited on the catalyst surface and in its bulk. Different regeneration reactions can be produced on the surface, namely:



The cases represented by eqs. (6), (7) and (8) have been presented elsewhere.¹⁴

The kinetics of equations (2)-(5) leads to the same conclusions¹⁴ when the concentration of oxygen was not enough to obtain CO₂.

For the case represented by equation (9) one obtains using eqs. (2)-(5) together with equation (9):

$$\frac{d[AX]}{dt} = k_1 P_A [X] - k_{-1} [AX] - k_3 [AX][OXX] \quad (11)$$

$$\frac{d[OXX]}{dt} = k_2 P_{O_2}^{1/2} [X]^2 - k_{-2} [OXX] - k_3 [AX][OXX] \quad (12)$$

$$\frac{d[CX]}{dt} = k_4 P_C [X] - k_5 [CX][OX] \quad (13)$$

where k_i , $i=1-5$ are the rate constants of the reaction mechanism.

If the concentration of O₂ molecules or O atoms are smaller than the concentration of CX compounds then the concentration of OX can be considered as a constant and k_5 replaced by k'_5 where $k'_5 = k_5 [OX]$. In these conditions, taking into considerations the free site conservation law and the Eigenberger's hypotheses^{15,16} presented previously¹⁴, one obtains:

$$[X] = 1 - [AX] - [CX] \quad (14)$$

Equations (11) and (12) take account for the variation of the fast variables while equation (13) described the behavior of the slow reactive adsorbed species. All these variables have a physical meaning as long as they are not negative and $x+y, z \leq 1$, where $x=[AX]$, $y=[OXX]$ and $Z=[CX]$.¹⁷

By considering the concentration into the form of fractional coverage and the equations (11)-(13) in a dimensionless form by dividing the constants k_i by k'_5 , a reduced system consisting of two differential equations, namely:

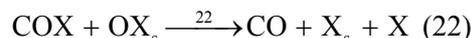
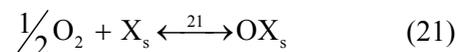
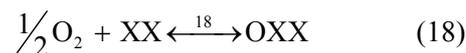
$$\frac{dx}{d\tau} = k_1^* P_A (1 - x - z) - k'_{-1} x - k'_{32} (1 - x - z)^2 \quad (15)$$

$$\frac{dz}{dt} = k'_4 (1 - x - z) \quad (16)$$

was obtained, where $\tau = k'_5 t$ and k'_i result from k_i .¹⁸ The obtained mathematical model contains now two autonomous ordinary differential equations: a cubic (equation (15)) and a linear one (equation (16)).

The case of surface regeneration represented by equation (10) leads, using the same procedure as before, to the same equations (15) and (16).

The cases presented in equations (2)-(5) are based on the hypotheses that the component A is different from the carbon C. But it can happen that A is the carbon atom C. In this case the kinetic model became:



As before the system of differential equations is:

$$\frac{d[CX]}{dt} = k_{17} P_C [X] - k_{-17} [CX] - k_{19} [CX][OXX] \quad (23)$$

$$\frac{d[OXX]}{dt} = k_{18} P_{O_2}^{1/2} [X] - k_{-18} [OXX] - k_{19} [CX][OXX] \quad (24)$$

$$\frac{d[X_s]}{dt} = k_{20} [X] - k_{-20} [X_s] - k_{21} P_{O_2}^{1/2} [X_s] + k_{22} [COX][OX_s] \quad (25)$$

The subsurface free site X_s is assumed to be formed due to the existence of defect catalysts structures. Also the rate constants for oxidation (21) and reduction (22) are much smaller than before. In these conditions, using the same hypotheses as for the previous systems these new equations can be reduced and described by equations (15) and (16).

The kinetic model presented before is based on the assumption of the reversible transformation of a free surface site in a free subsurface site.¹⁹

The steady state for the system eqs (15) and (16) can be obtained by solving a reduced cubic equation:

$$Y^3 + pX + q = 0 \quad (26)$$

as we have proved it earlier.^{14,18,20} The coefficients p and q are both functions of k_i' .^{18,20,21}

The mathematical analysis of the model described by equations (11)-(13) showed that oscillations are possible not only when the rate of carbon removal proceeds mainly by direct reactions with the gas phase oxygen,¹²⁻¹⁴ but also by the formation of a surface intermediates. The oscillations consist of periodic cycling between states of low and high reaction state. In the state of high reactivity the surface is covered by oxygen. In this part of oscillation the carbon obtained by a chemical reaction or by diffusion from the bulk prevails and the fraction of active site decreases. The reaction rate drops sharply to a low state of activity. The surface carbon formation is inhibited by the presence of adsorbed CO linearly bounded.²² By reaction with oxygen of the adsorbed CO or of a superficial compound with CO the fraction of active site increases until ignition occurs.

Most analytical systems of equations describing oscillatory reactions are two or three variable systems. The system presented in equations (11)-(13) is a three variable system. Using same valuable hypotheses the system can be reduced to a two variable system which offers advantages in using it: stable solutions, regular or damped oscillations, stable mode, focus or saddle points.^{18,20,21} This behavior is important for describing a lot of chemical models for oscillatory reactions²² because heterogeneous catalytic systems, used under atmospheric pressure, have some unique features: their local activity and transport properties are inherently non-uniform and the boundary conditions affect them because of the long range impact of the enthalpy balance.²⁴

Moreover, the interaction between the solid and fluid-phases can create and stabilize states, which would not exist in its absence.

The chemical models presented in this paper and elsewhere²³ belong either to a "black box" or to a class in which certain phenomena, no matter in what system it occurs, the models describing it are constructed.²⁴ In "black box" dynamical systems the inputs and outputs are able to be measured. Some chemical oscillations which present chaos can belong to this group.²⁶ Other chemical oscillations are described by models like "brusselator" or are "oregonator" for example. The transition to chaos via an infinite period – doubling bifurcation sentence can be modeled by a logistic map.^{27,28} It should be emphasized that the utility of such models is based on the oscillation theory laws,²⁵ which are general not depending on the concrete type of the studied system.

CONCLUSIONS

The carbon model can be an explanation for the appearance of chemical oscillations in reactions with compounds containing carbon atoms and could be modeled using a reduced cubic equation obtained with two kinetic models.

Acknowledgements. The authors gratefully acknowledged the support of the EU (ERDF) and Roumanian Government which approved acquisition of the research infrastructure under POS-CCE O 2.2.1 project INFRANANOCHEM - No. 19/01.03.2009.

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