ROLE OF THE NON-REACTIVE ADSORBED SPECIES IN THE HETEROGENEOUS CATALYTIC OSCILLATORY REACTIONS

Niculae I. IONESCU*

"Ilie Murgulescu" Institute of Physical Chemistry of the Roumanian Academy,
202 Splaiul Independentei, 060021 Bucharest, Roumania

An overall kinetic model is presented explaining the appearance of some kinetic instabilities in heterogeneous solid-gas systems. The model is based on adsorption-desorption phenomena and surface chemical reactions. The obtained results are discussed.

INTRODUCTION

By definition heterogeneously catalyzed reactions are systems far from thermodynamical equilibrium in which new phenomena – such as instabilities, oscillations, chemical waves or chaotic behavior – may develop. The investigation of the dynamic aspects of heterogeneous catalysis has yielded deep insight into the details of the kinetics of this reaction on a microscopic level as well as into the complexity of real reaction-diffusion systems at elevated pressure on a macroscopic level. At the same time the interest in oscillatory phenomena in catalytic reactions is caused by the possibility to perform such processes more efficiently using unsteady – state operations.

This explains the appreciable number of kinetic and mathematical models for explaining or simulating the appearance of oscillations.[1-8]

In our previous papers[9-15] we have developed an overall kinetic model for heterogeneous catalytic oxidations in oscillatory regime taking into account the balance of chemical species and simplifying the corresponding mathematical equations.

In the initial model there was one surface reaction between the reactants. The goal of this paper is to develop the model by considering the existence of two irreversible surface reactions of the reactants.

THE MODEL

Let now the reactions be:

$$A + B \xrightarrow{\ X\ } products \qquad (1)$$

which can be described by the following steps:

$$A + X \xleftrightarrow{\ 1\ } AX \qquad (2)$$

$$B + XX \xleftrightarrow{\ 2\ } BXX \qquad (3)$$

$$AX + BXX \xrightarrow{\ 3\ } AB + 3X \qquad (4)$$

$$BXX + A \xrightarrow{\ 4\ } AB + 2X \qquad (5)$$

$$B + X \xleftrightarrow{\ 5\ } BX \qquad (6)$$

In equations (1)-(6) A is a gaseous reactant, $B = 1/2\ O_2$ and X the free active sites of catalyst. The reactive adsorbed species of A and B are AX and BXX respectively and BX is a non reactive adsorbed species.

The model consists of five steps: two adsorption – desorption equilibria, a slow formation of a non-reactive adsorbed species and

---

* Corresponding author: ionescu@chimfiz.icf.ro

two irreversible surface chemical reactions followed both by a fast desorption of products. The relationship (6) which is also a surface reaction, being not in equilibrium with the fast steps of the mechanism, acts as a buffer of Eigenberger's type.[16] The sub-unitary coefficient of oxygen is necessary to reduce the rank of kinetic equations.[13]

In order to obtain an oscillatory behavior, the model needs two coupled paths via only one species, in this case the free active site *X*. The usual restriction for surface reaction models is the conservation of these free sites, which, in terms of fractional coverage's leads to:

$$\frac{d[AX]}{dt} = k_1[X] - k_{-1}[AX] - k_3[AX][BXX] \qquad (8)$$

$$\frac{d[BXX]}{dt} = k_2[X]^2 - k_{-2}[BXX] - k_3[AX][BXX] - k_4[BXX] \qquad (9)$$

$$\frac{d[BX]}{dt} = k_5[X] - k_{-5}[BX] \qquad (10)$$

where $k_1 = k_1' P_A$, $k_2 = k_2' P_{O_2}^{1/2}$, $k_5 = k_5' P_B$ and $k_4 = k_4' P_A$.

The system of equation (8)-(10) can be reduced with the assumptions used also in other papers.[9,10,14,15]

$$[BXX] = [AX], [BX] \qquad (11)$$

and

$$[BXX] \cong k_2[X]^2 / k_{-2} \qquad (12)$$

In these conditions relationship (7) becomes:

$$[X] = 1 - [AX] - [BX] \qquad (13)$$

Equations (8) and (9) account for the variation of fast variables while equation (10) describes the behavior of the slow variable which, in this case is the concentration of a non-reactive adsorbed species. All these variables have a physical meaning as long as they are not negative and $x + y$, $z \leq 1$ where $x = [AX]$, $y = [BXX]$ and $z = [BX]$.

Using the hypothesis that equilibrium is non-disturbed,[15] in this case equation (3) additional restrictions were imposed namely:

$$k_2 P_B, k_{-2} \gg k_3, k_4 \gg k_1 P_A, k_{-1}, k_5 P_B, k_{-5} \qquad (14)$$

By considering the concentrations into the form of fractional coverage and the equations in a dimensionless form by dividing the system (8)-(10)

$$[X] = 1 - [AX] - [BX] - 2[BXX] \qquad (7)$$

where *[X], [AX], [BX]* and *[BXX]* are the concentrations of free sites *X* and of *AX, BX* and *BXX* species respectively. The buffer step (6) is assumed to take place at a different lower time scale and the partial pressure in the gas phase is assumed to be constant.

The mathematical model of the kinetic model (2)-(6) is a non-linear system containing three ordinary differential equations namely:

by k_{-5}, using also the assumptions (11)-(14), one obtains a reduced system consisting of two differential equations namely:

$$\frac{dx}{d\tau} = k_1^*(1 - x - z) - k_{-1}^* x - k_{32} x(1 - x - z)^2 \qquad (15)$$

$$\frac{dz}{d\tau} = k_5^*(1 - x - z) - z \qquad (16)$$

where $\tau = k_{-5}t$, $k_i^* = k_i / k_{-5}$ with $i = 1$-5, $k_{-1}^* = k_{-1}/k_{-5}$ and $k_{32}^* = \dfrac{k_2 \cdot k_3}{k_2 \cdot k_{-5}}$.

The steady state of the system described by (15) and (16) can be obtained by solving the reduced cubic equation:

$$y^3 + py + q = 0 \qquad (17)$$

as we have proved earlier.[9,10,14,15]

By solving this reduced cubic equation (17) and analyzing the stability properties of the resulted steady state a lot of behaviors where obtained: stable solutions, regular or damped oscillations, stable node or focus and saddle point as presented elsewhere.[9,10]

The cubic equation (17) was obtained also in case of other kinetic models.[9, 10, 14, 15] This proves the importance and the validity of such an equation for the description of oscillatory heterogeneous reactions.

The theoretic framework for understanding these phenomena was developed in a branch of physics and mathematics – the non-linear dynamics. The name reflects the fact that the underlying mathematical equations have to be non-linear in order to reflect this type of behavior. The general structure of mathematical equations describing spatiotemporal pattern formation on a surface in case of system is that of a reaction-diffusion system having the one dimensional form:

$$\frac{\partial c_i}{\partial t} = F_i(\lambda, \boldsymbol{c}) + D_i \frac{\partial^2 c_i}{\partial x^2} \qquad (18)$$

In this equation $\boldsymbol{c}$ is a vector standing for the concentrations of the various chemical species and λ denotes a set of parameters such as temperature, pressure, etc. The kinetics of species i is contained in the term F_i, while the diffusion is considered in the usual Laplacian form in the second term, with D_i representing the diffusion coefficient. Assuming for simplicity that the surface reacts spatially homogeneously, the diffusion term vanishes and the system of partial differential equations reduces to a system of ordinary differential equations namely:

$$\frac{dc_i}{dt} = F_i(\lambda, \boldsymbol{c}) \qquad (19)$$

describing the local reaction kinetics.

Any realistic system requires, in principle, a large number of variables for its full description, but due to a separation of time and length scales, only a few of these many degrees of freedom are really important for the dynamics of the system.[6] Sometimes even only two of variables are sufficient, which in our case are *[AX]* and *[BX]*. Then, the system, after passing through the period of transient behavior can be in a stable state or it may exhibit sustained oscillations. By increasing the variable number from two to three, complex dynamical behavior becomes possible including deterministic chaos.

The observed rates are only a kind of a special case where a global synchronization mechanism produces macroscopic variations of the reaction rate. The more general case is that of some non-linear processes which take place on a local scale but are not visible to observations, since the seemingly trivial case of stationary rate is observed.

CONCLUSIONS

An overall kinetic model and the corresponding mathematical one were presented explaining the appearance of some instabilities in heterogeneous solid-gas systems. The model is based on adsorption-desorption equilibria, a slow formation of a non-reactive adsorbed species and two irreversible surface reactions followed both by a fast desorption of products. The obtained results are discussed.

REFERENCES

1. M.G. Slinko and M.M. Slinko, *Catal. Rev. Sci. Eng.*, **1978**, *17*, 119.
2. G. Ertl, *Adv. Catalysis,* **1990**, *37*, 213.
3. R. Imbihl, *Progr. Surf. Sci.,* **1993**, *44*, 185.
4. F. Schüth, B. E. Henry and L.D. Schmidt, *Adv. Catalysis*, **1993**, *39*, 51.
5. M.M. Slinko and N.I. Jaeger, "Oscillatory Heterogeneous Catalytic Systems, Studies in Surface Science and Catalysis", Elsevier, 1994, vol. 86.
6. R. Imbihl and G. Ertl, *Chem. Rev.,* **1995**, *95*, 697.
7. R. Imbihl, *Catal. Today*, **2005**, *105*, 206.
8. V.V. Gorodetskii, V.I. Elokhin, J. W. Baker and B.E. Nieuwenhuys. *Catal. Today,* **2005**, *105*, 183.
9. N.I. Ionescu and T. Danciu, *React. Kinet. Catal. Lett.*, **1992**, *47*, 105.
10. N.I. Ionescu and T. Danciu, *Rev. Roumaine Chim.*, **1993**, *38*, 783.
11. N.I. Ionescu and T. Danciu, *React. Kinet. Catal. Lett.*, **1995**, *54*, 121.
12. T. Danciu, N.I. Ionescu and E. I. Segal, *Rev. Roumaine Chim.*, **1997**, *42*, 455.
13. T. Danciu and N.I. Ionescu, *Rev. Roumaine Chim.*, **1999**, *44*, 181.
14. N.I. Ionescu, *Rev. Roumaine Chim.*, **2009**, *54*, 339.
15. N.I. Ionescu, *Rev. Roumaine Chim.*, **2010**, *55*, 349.
16. G. Eigenberger, *Chem. Eng. Sci.*, **1978**, *33*, 1263.