ROLE OF THE THIRD ADSORBED SPECIES IN THE HETEROGENEOUS CATALYTIC OSCILLATORY REACTIONS

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Two overall kinetic models with three adsorbed species can explain the appearance of some kinetic instabilities in heterogeneous catalytic solid-gas systems. The models are based on three adsorption-desorption phenomena and one or two surface chemical reactions. The obtained results are discussed.

INTRODUCTION

The understanding of the kinetics of heterogeneous catalytic reactions is of interest, due the importance of heterogeneous catalysis in the chemical industry. The great interest of self-oscillatory phenomena is caused by the possibility to perform the catalytic processes more efficiently using unsteady-state conditions. Experimental studies in this field are based on sophisticated physical methods developed in surface science and solid state physics. Now chemists, chemical engineers, physicists and experts in non-linear science are interested to investigate these reactions. This explain the fact that an appreciable number of kinetic and mathematical models for the simulation of oscillations can be found in the literature. [1-9]

Reaction models oftenly used to explain heterogeneously catalysed oscillatory reactions are based on Langmuir-Hinshelwood – and/or Eley-Rideal mechanisms. Both models describe microscopic events and combine a great number of apparently independent elementary reactions to result in equations for the macroscopically observed reaction rates.

In our previous papers[10-17] we have developed overall kinetic models for heterogeneous catalytic oxidation reaction taking into account the balance of chemical species, the participation of the subsurface oxygen in reaction or the existence of two irreversible surface reactions of the reactants.

The goal of this paper is to develop a model in which three different reactants are present on the catalyst surface.

THE MODEL

The proposed model implies three different reactants and is formed of four steps: three adsorption – desorption equilibria and one reaction between two adsorbed species which was considered entirely displaced. The products desorption was a fast one.

Let now the reaction be:

$$A + B \xrightarrow[D]{X} products \tag{1}$$

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which can be described by the following steps:

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

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

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

$$D + X \xleftrightarrow{\ 4\ } DX \qquad (5)$$

In equations (1)-(5) A and D are gaseous reactants, $B=1/2O_2$, X is a free active site of the catalysts surface, AX and BXX the reactive adsorbed species of A and B and DX the adsorbed species of D which can act as a buffer step of the system.

The kinetic model (2)-(5) is formed by two parts. The first part consists of three steps: two adsorption-desorption equilibria and an irreversible surface chemical reaction of Langmuir-Hinshelwood's type. The second part consists only of one step: the reversible adsorption of another gas D which competes with A for the free sites X and acts as a buffer of Eigenberger's type.[18,19]

In order to obtain an oscillatory behavior the model needs two coupled paths via only one species.[20] This species can be Pd and Pt atoms[6,8,20-37] or the free active site X.[20] From the kinetic model (eqs. (2) to (5)) the following non-linear system containing three ordinary differential equations was obtained namely:

$$\frac{d[AX]}{dt} = k_1 P_A X - k_{-1}[AX] - k_3[AX][BXX] \quad (6)$$

$$\frac{d[BXX]}{dt} = k_2 P_B[X]^2 - k_{-2}[BXX] - k_3[AX][BXX] \quad (7)$$

$$\frac{d[DX]}{dt} = k_4 P_D[X] - k_{-4}[DX] \qquad (8)$$

where k_i are the rate constants of the reaction mechanism.

The non-reactive species DX is a more stable combination of the catalyst with oxygen. At the same time, the irreversible surface reaction (4) is followed by a very fast desorption.

The site conservation equation in terms of fractional coverages is:

$$[X]=1-[AX]-2[BXX]-[DX] \qquad (9)$$

Also the rank of the system (6) to (8) can be reduced using the assumptions:[18,19]

$$[BXX] \ll [AX], \ [DX] \text{ and}$$
$$[BXX] \cong k_2[X]^2 / k_{-2} \qquad (10)$$

In these conditions equation (9) remains:

$$[X]=1\text{-}[AX]\text{-}[DX] \qquad (11)$$

The rank of the differential equations can be reduced using the Eigenberger's hypothesis too.[18,19] which imposes additional restrictions. These restriction are:

$$k_2 P_B, k_{-2} \gg k_3 \gg k_1 P_A, k_{-1}, k_4 P_D, k_{-4} \quad (12)$$

Considering the equations (6)-(8) in a dimensionless form by dividing the system by k_{-4} the concentrations in the form of fractional coverage and using equations (11) and (12) one obtains:

$$\frac{dx}{d\tau} = k_1^* P_A(1 - x - z) - k_{-1}^* x - k_{32}^* P_B x(1 - x - z)^2 \quad (13)$$

$$\frac{dz}{d\tau} = k_4^* P_D(1 - x - z) - z \qquad (14)$$

where $\tau = k_{-4}t, k_i^* = k_i / k_{-4}$ with $i=1$-4,

$k_{-1}^* = k_{-1} / k_{-4}$ and $k_{32}^* = \dfrac{k_2 k_3}{k_{-2} k_{-4}}$.

All the variables of equations (13) and (14) have a physical meaning as long as they are not negative in the region R where they have been studied and $R \{x,z; x \geq 0; z \geq 0; x + z \leq 1\}$ with $x = [AX]$ and $z = [DX]$.

In such a way the system (6)-(8) is reduced to the system (13)-(14) consisting of two autonomous ordinary differential equations, a cubic, equation (13) and a linear equation (14).

The steady state for the system of eqs (13) and (14) can be obtained by solving a reduced cubic equation as the result of the substitution of equation (14) into equation (13), both in homogeneous form and changing the variable x by:

$$x = y\text{-}2/3$$

The final equation is:

$$y^3 + py + q = 0$$

where the coefficients p and q are both different functions of k_1^*, k_{-1}^*, k_{32}^* and k_4^* as presented else where .[10, 11]

Solving this reduced cubic equation (16) a lot of behaviors were obtained: stable solutions,

regular or damped oscillations, stable node, focus or saddle points. [10,11]

But it can happen that the *A* molecules react with the adsorbed compound *DX*. In this case, with the addition of an Eley-Rideal step, the system becomes:

$$A + X \xleftrightarrow{\ 1\ } AX \tag{17}$$

$$B + XX \xleftrightarrow{\ 2\ } BXX \tag{18}$$

$$AX + BXX \xrightarrow{\ 3\ } AB + 3X \tag{19}$$

$$D + X \xleftrightarrow{\ 4\ } DX \tag{20}$$

$$A + DX \xrightarrow{\ 5\ } AD + X \tag{21}$$

The non-linear system containing also three ordinary differential equations was quite the same with the system (6)-(8) with the difference that for the last equation of the system (8) one obtains the form:

$$\frac{d[DX]}{dt} = k_4 P_D X - k_{-4}[DX] - k_5 P_A[DX] \tag{22}$$

Using the same notations as before one obtaines:

$$\frac{dz}{d\tau} = k_4^*(1-x-z) - z - k_5^* P_D z = k_4^*(1-x-z) - z(1+k_5^* P_A) \tag{23}$$

where $k_5^* = k_5 / k_{-4}$

Assuming that the Eley-Rideal mechanism is less important than the Langmuir-Hinshelwood mechanism in the appearance of oscillations $(k_5 \ll k_i)$ it results that the term $k_5^* P_A$ can be neglected. In these conditions equation (23) is the same as equation (14) and the system can be easily solved leading to a reduced cubic equation.

Several possible feedback mechanisms have been suggested to describe experimental data on kinetic oscillations. One of them is the dependence of reaction rate upon the vacant site on the catalyst surface.[5] This type of feedback mechanism proposed by Eigenberger[18,19] was used by us in our previous papers[9-17] as well as in the present one. The mechanism emphasized that the competition of *A, B* and *D* for the same type of active sites on the catalyst surface is responsible for the observed oscillations. These oscillations can be interpreted as a periodic successions of ignited and extinguished states. The extinction is connected with the depletion of empty active sites due to the blocking chemisorptions of reaction.[5] During the ignition, the vacant sites are set free and accelerate

the reaction. A periodic succession of ignited and extinguished states can therefore be possible if a buffer or a storage are available which provide empty sites after the reaction of ignition takes place.[5] The general form of the buffer step is represented by equation (5) of the system which is also valid in case of only two components, *A* and *B*. The only restrictions is that *[DX]* or *[BX]* are either not involved or are only slightly involved in a surface reaction. The constants of adsorption and desorption of *D* or *B*, in case of three components, have to be small compared to the constants of mechanism represented by equation (2)-(4) to be sure that the buffer step becomes effective after the ignition and extinction of the reaction.[18,19]

The reduced cubic equation (16) represents well unstable behaviors not only in cases with two[9-15] or three reactants, but also in cases with two reactants and the presence of subsurface oxygen[16] or the existence of two irreversible surface reactions [17] in a two component system.

In modeling oscillations two essential aspects have to be taken into consideration: on the microscopic level to find the smallest unit, which is capable to oscillate and on the macroscopic level to find the global synchronization mechanisms which 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

Two overall kinetic models and the corresponding mathematical ones were presented and can explain the appearance of some instabilities in heterogeneous catalytic solid-gas systems. The models are based: the first on the presence of three reactants and the second one on a reaction of the first component with the third one. 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. D. Luss and M. Sheintuch, *Catal. Today*, **2005**, *105*, 254.
10. N.I. Ionescu and T. Danciu, *React. Kinet. Catal. Lett.*, **1992**, *47*, 105.
11. N.I. Ionescu and T. Danciu, *Rev. Roum. Chim.*, **1993**, *38*, 783.
12. N.I. Ionescu and T. Danciu, *React. Kinet. Catal. Lett.*, **1995**, *54*, 121.
13. T. Danciu, N.I. Ionescu and E. I. Segal, *Rev. Roum. Chim.*, **1997**, *42*, 455.
14. T. Danciu and N.I. Ionescu, *Rev. Roum. Chim.*, **1999**, *44*, 181.
15. N.I. Ionescu, *Rev. Roum. Chim.*, **2009**, *54*, 339.
16. N.I. Ionescu, *Rev. Roum. Chim.*, **2010**, *55*, 349.
17. N.I. Ionescu, *Rev. Roum. Chim.*, (*in press*)
18. G. Eigenberger, *Chem. Eng. Sci.*, **1978**, *33*, 1255.
19. G. Eigenberger, *Chem. Eng. Sci.*, **1978**, *33*, 1263.
20. U. F. Franck, *Ber. Bunsenges. Phys. Chem.*, **1980**, *84,* 334.
21. P.A. Carlsson, V.P. Zhdanov and M. Skoglundh, *Phys. Chem. Chem. Phys.*, **2006***, 8*, 2703.
22. N.I. Jaeger, K. Möller and P.J. Plath, *J. Chem. Soc., Faraday Trans*. I, **1986**, *82*, 3315.
23. N.I. Ionescu, M.S. Chirca and D.I. Marchidan, *Rev. Roum. Chim.*, **1986**, *31*, 671.
24. N.I. Ionescu, M.S. Chirca and D.I. Marchidan, *React. Kinet. Catal. Lett.*, **1986**, *31*, 361.
25. N.I. Ionescu, M.S. Chirca and D.I. Marchidan, *Proc. 6th Intern. Symp. Heterogeneous Catalysis,* Sofia*,* 1987, vol. 1, p. 25.
26. N.I. Ionescu, M.S. Chircă and D.I. Marchidan, *React. Kinet. Catal. Lett.,* **1989**, *38*, 249.
27. M.M. Slinko, N.I. Jaeger and P. Svensson*, J. Catalysis*, **1989**, *118*, 349.
28. N.I. Ionescu, M.S. Chircă and D.I. Marchidan, *Rev. Roum. Chim.*, **1991**, *36*, 809.
29. P.J. Plath, N.I. Ionescu, M.S. Chircă, N.I. Jaeger, M.A. Liauw and U. Sydow, *React. Kinet. Catal. Lett.*, **1994**, *53*, 391.
30. N.I. Jaeger, M. A. Liauw and P.J. Plath, *J. Chem. Phys.*, **1996**, *104*, 6375.
31. M.M. Slinko, E. S. Kurkina, M.A. Liauw and N.I. Jaeger, *J. Chem. Phys.*, **1999**, *111*, 8105.
32. N.I. Ionescu, N.I. Jaeger, P.J. Plath and M.A. Liauw, *J.Therm. Anal. Cal.,* **2000**, *61*, 995.
33. N.I. Ionescu, N.I. Jaeger, P.J. Plath, M.A. Liauw and C. Hornoiu, *J. Therm. Anal. Cal.*, **2003**, *73*, 851.
34. N.I. Ionescu, M. Căldăraru, C. Hornoiu and C. Munteanu, *Rev. Roum. Chim.*, **2005**, *50*, 985.
35. N.I. Ionescu, M. Căldăraru, C. Hornoiu and C. Munteanu, *React. Kinet. Catal. Lett.*, **2007**, *91*, 257.
36. N.I. Ionescu, N.I. Jaeger, P.J. Plath and C. Hornoiu, *J. Therm. Anal. Cal*., **2008**, *91*, 381.
37. N.I. Ionescu, N.I. Jaeger, P.J. Plath and C. Hornoiu, *Rev. Roum. Chim.*, **2010**, *55*, 105.