# ROLE OF TIME SCALES IN HETEROGENEOUS CATALYTIC OSCILLATORY REACTIONS

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An overall kinetic model is presented which explains the appearance of some kinetic instabilities in heterogeneous catalytic reactions. The model is based on different time scales for the reactions of the model. The obtained results are discussed.

$$A + B \longrightarrow products$$
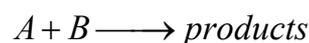
Heterogeneous catalytic reactions are non-linear multilevel chemical reaction systems far from thermodynamical equilibrium which exhibit complex temporal behavior such as instabilities oscillations, chemical waves or chaos.[1-12] Oscillatory behavior can be obtained on various levels of a heterogeneous catalytic system. The first level is an element on a single crystal surface or a single metal cluster which can be described by a kinetic point model. The second level is an inhomogeneous single crystal surface or a pellet on a supported catalyst and the third level a polycrystalline metallic surface or a catalyst bed. From the second level up each level must be considered as an array of local oscillators. The observed temporal behavior depends not only upon the properties of the local oscillators on each level but also upon the strength and the nature of the coupling between them.[13,14] The global oscillation requires the coupling of a large number of microscopic oscillators. The surface of a catalyst bed may be viewed as an array of oscillators coupled with each other locally via heat transfer, surface diffusion or gas phase.[13]

The appreciable number of kinetic and mathematical models for the explanation of oscillations are mainly based on Langmuir-Hinshelwood and/or Eley-Rideal mechanism. Both models describe microscopic events and combine a great number of apparently independent elementary reactions to obtain the equations for the macroscopically observed reaction rates.

In our previous papers[15-23] we have developed overall kinetic models for heterogeneous catalytic oscillatory reactions taking into account the balance of chemical species, the participation of the subsurface oxygen in reaction, the existence of three different reactants, the role of the adsorbed carbon or two irreversible surface reactions of the reactants.

The goal of this paper is to develop model taking into account different time scales for a oscillatory reaction.

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THE MODEL

Let the reaction be:

$$A + B \longrightarrow products \tag{1}$$

which can be described by the following steps:

$$A + S \xleftrightarrow{\;1\;} AS \tag{2}$$

$$B + SS \xleftrightarrow{\;2\;} BSS \tag{3}$$

$$AS + BSS \xrightarrow{\;3\;} AB + 3S \tag{4}$$

$$B + S \xleftrightarrow{\;4\;} BS \tag{5}$$

In equations (1)-(6) A and B are gaseous reactants, S is a free active site of the catalyst surface, AS and BSS the reactive adsorbed specie of A and B and BS the adsorbed species of B which is a non reactive one and can acts as a buffer step of the system.

From the kinetic model (eqs. (2) to (5)) the following non-linear system containing three ordinary differential equations was obtained namely:

$$\frac{d[AS]}{dt} = k_1[S] - k_{-1}[AS] - k_3[AS][BSS] \tag{6}$$

$$\frac{d[BSS]}{dt} = k_2[S]^2 - k_{-2}[BSS] - k_3[AS][BSS] \tag{7}$$

$$\frac{d[BS]}{dt} = k_4[S] - k_{-4}[BS] \tag{8}$$

where $k_1 = k_1' P_A$, $k_2 = k_2' P_B$ and $k_4 = k_4' P_B$, k_i' being the rate constants of the reaction mechanism.

In order to obtain an oscillatory behavior, the model needs two coupled path[24] via only one specie which in this case is the free active site S.

All the variables of this system have a physical meaning as long as they are not negative and $x+y$, $z \leq 1$ where $x = [AS]$, $y = [BSS]$, $z = [BS]$.

An usual restriction of the superficial models is the conservation of free sites in term of fractional coverages:

$$[S] = 1 - [AS] - 2[BSS] - [BS] \tag{9}$$

or

$$S = 1 - x - 2y - z \tag{10}$$

The buffer-step, eq.(5) is assumed to take place at a slower time scale as the rest of equations.

The existence of a buffer step in the mechanism (eq.(5)) involves different time scales which offers the possibility to reduce the model without major changes[18,25] and some additional information could be obtained easier.[26]

From the kinetic equations (6)-(8) and (10) one obtains

$$\frac{dx}{dt} = k_1(1 - x - 2y - z) - k_{-1}x - k_3xy \tag{11}$$

$$\frac{dy}{dt} = k_2(1 - x - 2y - z)^2 - k_{-2}y - k_3xy \tag{12}$$

$$\frac{dz}{dt} = k_4(1 - x - 2y - z) - k_{-4}z \tag{13}$$

In order to eliminate one equation from the model, the stationarity principle was applied to eq. (12). Assuming now that $y << S$ it results for S and y^s:

$$S = 1 - x - z \tag{14}$$

and

$$y^s = \frac{k_2(1 - x - z)^2}{k_{-2} + k_3x} \tag{15}$$

y^s being the steady state value for y. Introducing eq. (15) in eq. (11) one obtains for the system:

$$\frac{dx}{dt} = k_1(1 - x - z) - k_{-1}x - k_3x \; \frac{k_2(1 - x - z)^2}{k_{-2} + k_3x} \tag{16}$$

$$\frac{dz}{dt} = k_4(1 - x - z) - k_{-4}z \tag{17}$$

The dynamic behavior of the system represented by eq. (16) and (17) can be described by a determinate two-dimensional dynamical system namely:

$$\varepsilon \dot{x} = f(x, z, \vec{k})$$

$$\dot{z} = g(x, z, \vec{k}) \tag{18}$$

with one slowly and one rapidly changing variable z and x respectively, $\vec{k}$ being the vector of external parameters. In the $\varepsilon \to 0$ limit, system (18) will be the simplest mathematical model which accounts for the dynamic features.[27] The experimental condition linked to system (18) is that the shape of oscillations must present

sufficiently separate time scales, at least in the range of applied operating conditions.[27]

Taking into account the new value of S and the constant values for P_A and P_B, the system contains now only two variables. Dividing the equations (16) and (17) with k_{-4} it results the normalization of the entire system which becomes in a dimensionless form:

$$\varepsilon \, \dot{x} = k_1^*(1-x-z) - k_{-1}^* x - k_{32}^* \frac{x(1-x-z)^2}{k_{-2}+k_3 x} \quad (19)$$

$$\dot{z} = k_4^*(1-x-z) - z \quad (20)$$

where $\dot{x} = \dfrac{dx}{d\tau}$; $\quad \dot{z} = \dfrac{dz}{d\tau}$; $\quad \tau = k_{-4}t$; $\quad k_1^* = \dfrac{k_1}{k_{-4}}$;

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

A system similar with the system (19) was obtained earlier[15-23] taking into account the hypothesis of a non-disturbed equilibrium.[28-30] This case, when different time scales are considered, leads to quite the same equations with the difference of using y^s instead of y.

This form introduces a supplementary term in the denominator of eq. (20). Using the restriction $k_{-2}+k_3x<<01$ the system is the same with the system which was obtained earlier.[15-23] This last system was analyzed solving a reduced cubic equation:

$$Y^3 + pY + q = 0 \quad (21)$$

when the coefficient p and q are different functions of the constants k_i^* as presented elsewhere.[15,16] Solving this reduced cubic equation (21) many behaviors were obtained: steady-state, regular or damped oscillations, stable mode, focus or saddle points.[15,16]

The mathematical model presented in eq. (19), (20) and (21) accounts for the sequence of transitions and divides the parameters space into regions with qualitatively types of behavior.

The stable dynamical system given by equations (18) are characterized by a phase plane behavior which is stable under small perturbations of the external parameters k_i.

Normally $\varepsilon << 1$. But the cases when $\varepsilon \to 0$ can produce the disappearance of some details. At finite ε several existing behaviors of the system may be compressed in a single modification of the oscillatory behavior if ε becomes zero. The limiting model with $\varepsilon \to 0$ cannot predict the

parameter regions which exhibit all the fine structure of the sequences observed.

In case of oxidation reactions, the existence of two time scales may be explained by the different form of adsorbed oxygen: active or less active, both forms being essential for the oscillatory reaction.

For modeling oscillations two essential aspects have to be taken into consideration: on the microscopic scale to find the smallest unit which is capable to oscillate and on macroscopic level to find the global synchronization mechanism which produces macroscopic variation 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 for the explanation of instabilities in catalytic heterogeneous systems. The model is based on the existence of different time scales for the reactions of the system.

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