

KINETIC MODEL FOR HETEROGENEOUS CATALYTIC OSCILLATORY REACTIONS

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An overall kinetic model for the oscillatory catalytic oxidation reactions is presented. It is based on the balance of chemical species, the existence of subsurface oxygen and two time scales and can describe various type of unstable kinetic behaviors.

INTRODUCTION

Heterogeneous catalytic reactions are highly non-linear chemical systems that are operated far from equilibrium. In such systems new phenomena may develop such as instabilities, oscillations, chemical waves or chaotic behavior. Depending on the experimental conditions, which include also the design of the catalyst, such phenomena originate at various levels of the catalytic system ranging from the nm-scale on single crystal surfaces up to the macroscopic scale of a packed bed supported catalyst. The great interest of self-oscillatory phenomena in heterogeneous catalytic reactions is caused by the possibility to perform the catalytic processes more efficiently using unsteady-state operation conditions. This explains the fact that an appreciable number of kinetic and mathematical models for the simulation of oscillations can be found in the literature.¹⁻⁷

In our previous papers⁸⁻¹² we have developed an overall kinetic model for heterogeneous catalytic oxidation reactions taking into account the balance of chemical species and simplifying the corresponding mathematical equations. Many experimental studies on CO and lower alcohols oxidations on Pd-supported catalysts revealed that kinetic oscillations in such systems originate due to periodic oxidation-reduction of the Pd surface.¹³⁻²⁵ Based on these facts we try in this paper to extend this model taking into account the periodic

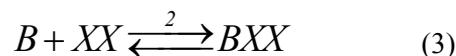
formation and removal on a metal surface of the subsurface oxygen in the course of an oscillatory oxidation reaction instead of considering the non-reactive adsorbed oxygen species as the buffer step of the model.

THE KINETIC MODEL

For the reaction:



the overall kinetic model is:



where A is the gaseous reactant, $B=1/2 O_2$, X = the free active sites of catalyst, AX and BXX the reactive adsorbed species of A and B and X_v , a subsurface site which can be occupied by oxygen atoms in the subsurface layer.

Subsurface oxygen can be formed by the diffusion of oxygen in to the metal lattice which is equivalent to the formation of a nonstoichiometric

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oxide.¹³ This oxide will be reduced by the reaction with the reactant A adsorbed on the surface, *i.e.*, the oxygen will diffuse back to the surface and the subsurface site become free for a new cycle.

The model consists of four steps: two adsorption-desorption equilibria, a slow subsurface oxygen formation and an irreversible surface chemical reaction of Langmuir – Hinshelwood's type followed by a fast desorption of products. The first three steps give a well balanced and self-consistent path. The second path consists only of step (5) which is a buffer of Eigenberger's type.²⁶ The sub-unitary coefficient of oxygen is necessary to reduce the rank of kinetic equation. Without this

coefficient a good balance of the overall process need an amplification of steps (2) and (4) which can induce complications.¹²

In order to obtain an oscillatory behavior the model needs two coupled paths via only one species.²⁷ In our case this species is the free site X which could denote Pd, Pt or Ir atoms. The free sites conservation, in term of fractional coverages, is:

$$[X] = 1 - [A-X] - 2[B-X-X] - [BXv] \quad (6)$$

The mathematical model of the kinetic model (2)-(5) is a non-linear system containing three ordinary differential equations:

$$\frac{d[AX]}{dt} = k_1[X] - k_{-1}[AX] - k_3[AX][BXX] \quad (7)$$

$$\frac{d[BXX]}{dt} = k_2[X]^2 - k_{-2}[BXX] - k_3[AX][BXX] \quad (8)$$

$$\frac{d[Xv]}{dt} = k_4B[X] - k_{-4}[BXv] \quad (9)$$

where $k_1 = k'_1P_A$ and $k_2 = k'_2P_{O_2}^{1/2}$.

The buffer step 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 system (7)-(9) can be reduced assuming the assumptions:^{26,27}

$$[BXX] \ll [AX], [Xv] \quad (10)$$

$$k_2P_{O_2}^{1/2}, k_2 \gg k_3 \gg k_1P_A, k_{-1}, k_4P_{O_2}^{1/2}, k_{-4} \quad (13)$$

These restriction allow us to reduce the rank of the ordinary differential equations (7)-(9).

By considering the concentrations into the form of fractional coverage and the equations in a

$$\frac{dx}{d\tau} = k_1^*P_A(1-x-z) - k_{-1}^*x - k_{32}^*x(1-x-z)^2 \quad (14)$$

$$\frac{dz}{d\tau} = k_4^*(1-x-z) - z \quad (15)$$

where $\tau = k_{-4}t$, $x = [A-X]$, $z = [BXv]$, $k_i^* = k_i/k_{-4}$ with $i=1,4$. $k_{-1}^* = k_{-1}/k_{-4}$ and

$$k_{32}^* = \frac{k_2 \cdot k_3}{k_{-2} \cdot k_{-4}}$$

and

$$[BXX] \cong k_2[X]^2/k_{-2} \quad (11)$$

With these conditions, eq. (6) becomes:

$$[X] = 1 - [AX] - [BXv] \quad (12)$$

The hypothesis of Eigenberger²⁶ that an equilibrium is non-disturbed, in our case eq. (3), imposes also the additional restrictions.^{3,11}

dimensionless form by dividing the system (7)-(9) by k_{-4} one obtains only a reduced system consisting of two differential equation namely:

The steady state of the reduced system (14) and (15) could be found by solving the non-linear equations:

$$\frac{dx}{d\tau} = 0 \quad (16)$$

$$\frac{dz}{d\tau} = 0 \quad (17)$$

This operation is equivalent with solving the reduced cubic equation:

$$y^3 + py + q = 0 \quad (18)$$

which results from the substitution of equation (17) in the form:

$$1 - x - z = (1 - x)/(1 + k_4^*) \quad (19)$$

into equation (16) and by changing the variable:

$$y = x - 2/3 \quad (20)$$

This model consists of one cubic differential equation (14) and a linear one (15). Such a mathematical model was also obtained by us⁸ by taking into account a non reactive species between the free surface site and oxygen.

The model has two different time scales, the slowest being represented by eq. (5), the formation of a subsurface site. In these conditions, using a mathematical procedure,²⁸ one could reduce the model with out major changes and the stability analysis becomes easier.

Solving this reduced cubic equation (18) a lot of behaviors were obtained: stable solutions, regular or damped oscillations, stable node or focus and saddle points. The unstable behaviors were presented elsewhere.^{8,18}

The mechanism of oscillations can be described as follows: starting with an oxidized surface, the adsorption of oxygen is less pronounced and the surface is covered mainly by the *A* molecules which reduce the surface. The number of free surface sites is increased and consequently the number of free subsurface sites is also increased and available for the interaction with oxygen. Adsorbed oxygen can penetrate into the subsurface layer and the concentration of this form of oxygen increases. As a result, the oxygen adsorption decreases and the surface becomes more free for the adsorption of the *A* molecules. Thus the oscillatory cycle can begin again. This mechanism is a form of the redox-mechanism,²⁹ which is general accepted for heterogeneous catalytic oxidation reactions³⁰ and has confirmations in experimental results.³¹ The oxidation (blocking) – reduction (reactivating) process is assumed to be driving force for the increasing and the decreasing branches of oscillations.^{1,15,31}

CONCLUSION

An overall kinetic model and the corresponding mathematical one is presented which can explain the appearance of the instabilities in a heterogeneous catalytic oxidation reaction. It is based on the balance of chemical species, two time scales and takes into account the existence of subsurface oxygen. The obtained results are discussed.

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