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SUBSURFACE OXYGEN INVOLVED IN KINETICS OF OSCILLATORY HETEROGENEOUS CATALYTIC REACTIONS

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An overall kinetic model is presented which explains the appearance of some kinetic instability in heterogeneous catalytic oxidation reactions. The model is based on the reactions of subsurface oxygen in the subsurface layer.

INTRODUCTION

Heterogeneous catalytic reactions are highly non-linear multilevel chemical reaction systems that are operated far from equilibrium. They are known to exhibit complex temporal behavior that has been in the focus of research of the non-linear dynamics systems. The intensive investigation of the dynamic aspects of heterogeneous catalysis has yielded deep insights into the details of the kinetic of these reactions. It became evident that the rate oscillations were the result of a self organization process on the catalytic surface and that the surface analytical tool and well-defined experiments and catalysts were required for understanding the mechanisms behind the oscillatory kinetics.[1-7]

The subsurface oxygen plays an increasing role, in the last time in the development of heterogeneous catalytic reactions in oscillatory regime. X-ray photoelectron spectroscopy (XPS), temperature programmed reaction (TPR) and molecular beam (MB) studies demonstrate the importance of O_{ads} diffusion in the lattice for the formation of the subsurface oxygen O_{sub} which is an important intermediate species in many oscillatory reactions.[8,9] This O_{sub} species is less active compared to O_{ads}.[10]

In our previous papers[11-15] 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 to the periodic oxidation-reduction on the Pd surface.[16-29] Based on these facts the model was extended[30] taking into account the periodic formation and removal of the subsurface oxygen.

The goal of this paper is to develop a model which accounts for the processes of reactants adsorption, reaction and desorption with the participation of subsurface oxygen.

THE MODEL

It its initial form[11] the model was proposed for the total oxidation of methanol over an industrial palladium catalyst. It was formed of four steps: three equilibrium of adsorption-desorption and a reaction between the adsorbed species which was considered entirely displaced. The desorption was a fast one,

Let now the reaction be:

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$$A + B \xrightarrow{\times} products \quad (1)$$

which can be described by the following steps:

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

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

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

$$X \xleftrightarrow{4} Xv \quad (5)$$

$$B + Xv \xrightarrow{5} BXv \quad (6)$$

$$BXv + AX \xrightarrow{6} AB + Xv + X \quad (7)$$

In equations (1)-(7) A is the gaseous reactant $B = 1/2\ O_2$, X is a free active site of catalyst, AX and BXX the reactive adsorbed species of A and B, Xv a subsurface site which can be occupied by oxygen atoms in the subsurface layer and BXv a subsurface oxygen compound.

The kinetic model (2)-(7) is formed by two parts. The first part which represents the surface reactions (2)–(4) the atomic oxygen route and the second one the subsurface oxygen route which is described by the reactions (5)-(7) in the subsurface layer 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 also of three steps: one the reversible formation of a vacant site in the subsurface layer and two irreversible reaction in which the vacant site of the subsurface layer is involved.

Subsurface oxygen is formed by the diffusion of oxygen into the metal lattice, in the outer layer of the metal.[16] This is equivalent to the formation of a nonstoichiometric oxide (step 6). This oxide will be reduced by reaction with the reactant A (step7) and the subsurface site becomes free for the new cycle.

For example, in case of CO oxidation on Pd surfaces, the feedback mechanism for oscillations is associated with the variations of the sticking probability of oxygen with the concentration of surface oxygen $O_{sub.}$[31] The oxide model[3] assumes that the O_{sub} layer simultaneously blocks oxygen adsorption leading to surface reactions which have a poisson effect on CO_2 formation. Nevertheless a slow reactions of CO_{ads} with O_{sub} removes the subsurface oxygen[32] and O_2 adsorption becomes possible again. Then, the subsurface oxygen layer starts to form again and the cycle is restored. The subsurface oxygen induces significant changes in the adsorption energy of $O_{ads.}$[33] The formation of O_{sub} takes place on the O_{ads} covered metal surface accompanied by a decrease of the sticking coefficient for oxygen adsorption. The transition to initial oxygen layer proceeds due to the increase of oxygen sticking coefficient due to the decrease of subsurface oxygen concentration.[10,31] The formation and removal of surface oxygen is the feedback mechanism of the reaction.

From the kinetic model (eqs. (2) to (7)) the following non-linear system containing three ordinary differential equations was obtained which describes the dynamic behavior of the adsorbed species and of the subsurface oxygen in the subsurface layer:

$$\frac{d[AX]}{dt} = k_1 P_A [X] - k_{-1}[AX] - k_3 [AX][BXX] - k_6 [AX][BX_v] \quad (8)$$

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

$$\frac{d[X_v]}{dt} = k_4 [X] - k_{-4}[X_v] - k_5 P_B [X_v] + k_6 [AX][BX_v] \quad (10)$$

where k_i are the rate constants of the reaction mechanism.

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

In order to obtain an oscillation behavior, a model needs two compled paths via only one specie.[34] In this case, taking into account experimental results on Pd[7,10] or Pt, [16-26] the free site X could be this specie.

The site conservation equation in terms of fractional coverages is:

$$[X]=1-[AX]-2[BXX]-[BX_v] \quad (11)$$

The rank of the system (8) to (10) could be reduced using the assumptions: [11]

$$[BXX] << [AX],\ [BX_v] \text{ and } [BXX] \cong k_2[X]^2/k_{-2} \quad (12)$$

and equation (11) becomes:

$$[X]=1-[AX]-[BX_v] \text{ or } S=1-x-z \quad (13)$$

where $S=[X]$.

The reaction rate constants for oxidation (k_5) and reduction (k_6) are much smaller rate constants compared to the constants for adsorption (k_1, k_2) desorption (k_{-1}, k_{-2}), surface reaction (k_3) and the formation of subsurface oxygen (k_4), as proved experimentally in CO oxidation on Pd.[16,19] In the same time the hypothesis of Eigenberger [36] that an equilibrium is non-disturbed, in this case equation (3) imposes also additional restrictions which allow to reduce the rank of the differential equations. These restriction are:

$$k_2 P_B, k_{-2} >> k_3 >> k_1 P_A, k_{-1}, k_4, k_{-4} \quad (14)$$

By considering the concentration into the form of fractional coverage, the equations (8) – (10) in a dimensionless form by dividing the system by k_{-4} and neglecting the terms containing k_5 and k_6 a reduced system consisting of two differential equations namely:

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

$$\frac{dz}{d\tau} = k_4^*(1-x-z) - z \quad (16)$$

are obtained where

$\tau = k_{-4}t, k_1^* = k_1 / k_{-4}, k_{-1}^* = k_{-1} / k_{-4}, k_{32}^* = \frac{k_2 k_3}{k_{-2} k_{-4}}$ and $k_4^* = k_4 / k_{-4}$

The mathematical model contains two autonomous ordinary differential equations: the former (equation (15)) is cubic, the latter (equation (16)) is linear. This model has four positive parameters $k_i^* > 1$.

The steady state of the system (eqs (15) and (16)) could be found by solving the reduced cubic equation:

$$Y^3 + pY + q = 0 \quad (17)$$

obtained by substitution of equation (16) into equation (15) in the form:

$$1-x-z = (1-x)/(1+k_4^*) \quad (18)$$

and changing the variable:

$$Y = x-2/3 \quad (19)$$

In equation (17) coefficients p and q are both different functions of $k_1^*, k_{-1}^*, k_{32}^*$ and k_4^* and were presented elsewhere.[11,12]

The discussion of equation (17) includes the multiplicity condition:

$$D<0 \quad (20)$$

D being the discriminant of equation (17).

If the condition (20) is satisfied, equation (17) has three real solutions, otherwise it has only one.

The stability analysis of the steady states could be obtained by using the Routh-Hurwitz criteria namely:

$$tr\ Y<0 \quad (21)$$

$$det\ Y>0 \quad (22)$$

where Y is the jacobian matrix of the system:

$$\frac{dx}{d\tau} = 0 \quad (23)$$

$$\frac{dz}{d\tau} = 0 \quad (24)$$

Violation of any conditions (21) and (22) yields to unstable behaviors: regular to unstable and saddle points that we have presented elsewhere.[11-15,30]

In chemical systems the chaotic behavior may be temporal or low dimensional chaos and spatiotemporal or high dimensional chaos.[36] The first type of chaos can be simulated with point models representing ordinary differential equations. The second one originates in distributed models and has to be simulated with partial differential equations. The model presented in equations (8)-(10) which describes kinetic surface oscillations does not produce chaos.

The observed rates are only a kind of a special case where a 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 the observations, since the seemingly trivial case of stationary rate is observed.[7] But in the last years, due to the improvement of experimental methods new oscillating heterogeneous catalytic systems have been discovered and summarized.[37]

The mechanism of regular 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 *A* molecules which reduce the surface. The number of free surface sites in the subsurface layer is also increased and are available for the interaction with oxygen. Adsorbed oxygen penetrates into the subsurface layer and the concentration of subsurface oxygen increases. The reaction of adsorbed *A* molecules with the subsurface oxygen removes this form of oxygen and the surface sites become now available for the adsorption of *A* and O_2 molecules. The subsurface oxygen layer starts to form and the cycle can begin again.

CONCLUSIONS

An overall kinetic model and the corresponding mathematical one where presented which explain the appearance of some instabilities in heterogeneous catalytic oxidation reactions. The model consists of two parts: the first one represents surface reactions and the second one reactions of the subsurface layer due to the subsurface oxygen. The obtained results are discussed.

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