



NOTE

ROLE OF THE ADSORBED CARBON IN HETEROGENEOUS CATALYTIC OSCILLATORY REACTIONS

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The model of adsorbed carbon can be a possible explanation of oscillations appeared in reactions with gaseous hydrocarbons. These oscillations can be explained kinetically by a reduced cubic equation. The obtained results are discussed.

The interest in self oscillatory phenomena produced in heterogeneous catalytic reactions is caused for a large part by the possibility to perform catalytic processes more efficiently using unsteady-state operations. The oscillations cycles of different products may have different forms and surface phases with respect to each other. This can produce valuable informations on the mechanism of such reactions.

The rate oscillations are only a kind of synchronization mechanism of individual oscillators, which produced macroscopic variation of the reaction rate. The general case is that of some non linear processes which take place on a local scale but are not visible to the outside, since the seemingly trivial case of a stationary rate is normally observed. Exploring such phenomena is in fact essential for understanding heterogeneous catalysis. This explain the great number of kinetic and mathematical models existing for the simulation of oscillations.¹⁻¹¹ In the last years, due to the improvement of experimental and theoretical methods, new oscillating heterogeneous catalytic system have been discovered and summarized.¹²

When one of the reactant is a gaseous hydrocarbon it happens that due to pyrolysis

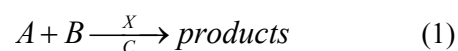
processes carbon may be obtained and deposited on the catalyst surface and in its bulk.

In this case a slow catalyst deactivation occurs which can be a cause of producing chemical oscillations.^{13,14} The carbon deposition and the regeneration of the deactivated sites by oxidation represent the buffer step present in an oscillation.

In our previous papers¹⁵⁻²³ we have developed an overall kinetic model for heterogeneous catalytic reactions taking into account the balance of chemical species and simplifying the corresponding mathematical equations. In its initial form the model was proposed for the total oxidation of methanol over an industrial palladium catalyst.^{15,16} The goal of this paper is to see if our model can explain the appearance of oscillations due to the adsorbed carbon on a catalytic surface.

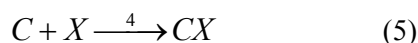
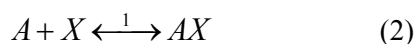
THE MODEL

Let now the reaction be:



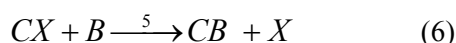
which, in case of the carbon presence, can be described by the following steps:

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In equations (1)-(5) A and B are a gaseous reactants, C the carbon impurity, X a free active site of the catalyst surface, AX and BXX are the reactive adsorbed species of A and B and finally CX is the adsorbed specie of carbon, involved in the buffer step of the system.

Because the specie CX is irreversible adsorbed on the surface, the catalyst can be regenerate from its deactivation state by oxidation with oxygen. That is why the next equation:



The kinetic model (2)-(6) is formed by two parts. The first one consists of three steps: two adsorption-desorption equilibria and an irreversible surface chemical reaction of Langmuir-Hinshelwood's type. The second part consists of two irreversible steps: the adsorption of carbon C on the surface, which competes with A and B for the free sites X and a reaction of Rideal's type of the adsorbed carbon with oxygen. The desorption of the products was assumed to be a fast one.

In order to obtain an oscillatory behavior the model needs two coupled paths via only and species which, in this case is the free active site X .²⁴ From the kinetic model, eqs (2) to (6), the following mathematical non-linear system containing three ordinary differential equations was obtained:

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

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

$$\frac{d[CX]}{dt} = k_4 P_C [X] - k_5 P_B [CX]$$

where k_i with $i=1-5$ are the rate constants of the reaction mechanism.

The free site conservation equation in terms of fractional coverage's leads to:

$$[X] = 1 - [AX] - 2[BXX] - [CX] \quad (8)$$

Taking into account the Eigenberger's hypothesis^{25,26} that an equilibrium is almost non-disturbed, in this case step (3) the additional restrictions were imposed:

$$k_2 (P_B)^{1/2}, k_{-2} \gg k_3 \gg k_1 P_A, k_{-1}, k_4 P_C, k_5 P_B \quad (9)$$

Although disputable²⁷ the restriction (9) is very attractive for the mathematical treatment because it simplifies the balance (8) which together with the assumptions:

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

becomes:

$$[X] = 1 - [AX] - [CX] \quad (11)$$

In the same time, this restriction reduces the rank of the ordinary differential equations.

By considering the concentration into a form of fractional coverage and the equation (7) in a dimensionless form by dividing the system by $k_5 P_B$ a reduced system consisting of two differential equations namely:

$$\frac{dx}{d\tau} = k_1^* P_A (1 - x - z) - k_{-1}^* x - k_{32}^* x (1 - x - z)^2 \quad (12)$$

$$\frac{dz}{d\tau} = k_4^* (1 - x - z) - z \quad (13)$$

was

obtained

when

$$\tau = k_5 P_B t, k_1^* = \frac{k_1}{k_5 P_B}, k_{-1}^* = \frac{k_{-1}}{k_5 P_B}, k_4^* = \frac{k_4}{k_5 P_B} \quad \text{and}$$

$$k_{32}^* = \frac{k_2 k_3}{k_{-2} k_5 P_B}$$

The mathematical model contains now two autonomous ordinary differential equation a cubic (equation (12)) and a linear one (equation (13)).

All the variables of equation (12) and (13) 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 $z = [CX]$.

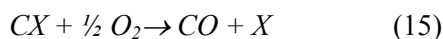
The steady state of the system (12) and (13) can be obtained by solving the reduced cubic equation.

$$y^3 + py + q = 0 \quad (14)$$

as we have proved earlier.^{15,16,20-23} The coefficients p and q are both functions of k_i^* as presented elsewhere¹⁵⁻¹⁷.

Solving this reduced cubic equations a lot of behaviors were obtained: stable solutions, regular or damped oscillations, stable nod, focus or saddle points.^{15,16}

If that the concentration of oxygen is not enough to obtain CO₂ then:



This last equations must be added to the former system. The conclusions are the same with the observation that $k_5 P_B$ must be replaced by $k_5'' P_{O_2}^{1/2}$.

The oscillations consist of periodic cycling between states of low and high reaction rates.^{28,29} When the diffusion of carbon from the bulk prevails, the fraction of active site decreases till to a critical value and the reaction rate drops sharply to a low state of activity. In this case the surface is covered by CO molecules linearly bounded.²⁹ In the state of high reaction rate the surface is covered by a substantial amount of oxygen as revealed by IR-reflectance spectroscopy.²⁹ The surface carbon formation is inhibited by the presence of adsorbed CO and the fraction of active sites increases until ignition occurs and the cycle is repeated.

This carbon model opens also some discussions. The high CO coverage is typically found with low reaction state, implying a low coverage of oxygen.⁵ This makes it difficult to imagine that C atoms could be easily removed in a low-reaction-rate state. The temperature required for carbon combustion are higher than those for which oscillatory CO oxidation on Pt have been observed.⁶ Also the rate of carbon diffusion from the bulk seems to be too slow to guarantee the observed period of oscillations. Nevertheless, the carbon model, which is supported by some experimental evidence remains a possible explanation for oscillations, at least at atmospheric pressure.

The reduced cubic equation (14) represents well unstable behaviors not only in cases with two¹⁵⁻¹⁷ or three reactants on the surface, but also in the presence of subsurface oxygen,^{10,21} the existence of two irreversible reactions on the surface²² or in the presence of a non-reactive adsorbed species on the surface.²³ In the present case this equation was proved in a system with four or five different reactants on the surface.

The carbon model belongs to the group of isothermal models which have been obtained in the approximations that the lateral interactions of adsorbed molecules are not taken into consideration and high surface mobilities are

assumed. These models use Langmuir-Hinshelwood or Eley – Rideal mechanism or sometimes both mechanisms together.

In modeling oscillations two essential aspects have to be considered: on the microscopic level to find the smallest unit which is capable to oscillate and on macroscopic scale to find the global synchronization mechanism which produces the macroscopic variations of the reaction rate.

There are three different mechanisms that can act as a synchronization force.⁵ These mechanisms are thermal synchronization through the catalyst, through its support or the gas phase.⁵ Other possible mechanisms on the catalyst surface are the surface diffusion of the adsorbed species or the phase transition of the surface structure.³⁰ Which of these processes are dominant depend on the individual system.

CONCLUSIONS

The carbon model is one of the possible explanation of the appearance of oscillations in reactions with gaseous hydrocarbons. These systems can be described kinetically by a reduced cubic equation which explains also other instabilities in heterogeneous solid-gas systems.

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