



*Dedicated to the memory of
Professor Victor-Emanuel Sahini (1927–2017)*

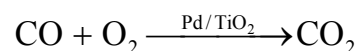
OSCILLATIONS IN THE SYSTEM CO/CATALYTIC SURFACE

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A model which explains the oscillations obtained during the oxidation of CO on Pd/TiO₂ catalyst have been presented. The model is based on two forms of free active sites of the catalyt.



INTRODUCTION

Heterogeneous catalytic reactions are non-linear multilevel chemical reaction systems far from thermodynamic equilibrium which exhibit complex temporal behavior such as instabilities, oscillations, chemical waves or chaos.^{1,2} The oscillations cycles of different products may have different forms and surface phases with respect to each other. These facts can produce valuable information on the kinetics and mechanism of these reactions. This explain also great number of kinetic and mathematical models for modeling or simulation the chemical oscillations,²⁻¹⁰ in isothermal and non-isothermal conditions.¹¹⁻¹⁶

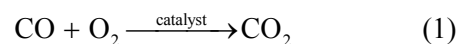
Carbon monoxide is a toxic, colorless and odorless gas undetectable by human beings. That is why a particular attention has been paid in the recent years to the detection and the removal of carbon monoxide from the environment, particularly the atmosphere. The main solution was its removing from air by oxidation. Therefore, many studies have been focused on the CO oxidation over metal oxides catalyts.^{17,18}

Titanium dioxide has been extensively studied due to its properties: stability, non-toxicity and low cost. It is used as gas sensing material and in catalysis, especially as photocatalyst.¹⁹ Pd dispersed on high surface area metal oxides are typical combustion catalyts.^{20,21}

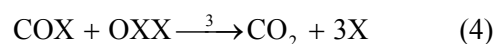
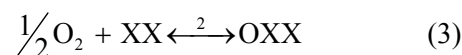
The goal of this paper is to present an isothermal kinetic model explaining the oscillations obtained during the interaction of CO with a Pd/TiO₂ surface.

THE MODEL

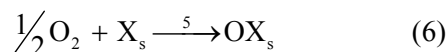
Let now the reaction be:



which can be described by the following steps:



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where X is a free active surface site and X_s a free active subsurface site. COX and OXX are the reactive adsorbed species of CO and oxygen involved in the reaction step of the system.

The kinetic model (2)-(7) 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 of one irreversible step, the

transformation of the free active site into on free under the surface site, on another one the reaction of the subsurface site with oxygen the last step being the reaction of adsorbed CO with the adsorbed subsurface oxygen. The last three steps describe the periodic formation and removal of a subsurface site in the course of the reaction with adsorbed CO molecules. 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 one specie.²² From the kinetic model (eqs (2) to (7)) the following non-linear systems containing three ordinary differential equation was obtained, namely:

$$\frac{d[COX]}{dt} = k_1 P_{CO} [X] - k_{-1} [COX] - k_3 [COX][OXX] - k_6 [COX][OX_s] \quad (8)$$

$$\frac{d[OXX]}{dt} = k_2 P_{O_2}^{1/2} [X]^2 - k_{-2} [OXX] - k_3 [COX][OXX] \quad (9)$$

$$\frac{d[X_s]}{dt} = k_4 [X] - k_{-4} [X_s] - k_5 P_{O_2}^{1/2} [X_s] - k_6 [COX][OX_s] \quad (10)$$

where k_i , $i=1-6$ are the rate constants of the reaction mechanism.

Subsurface site X_s is formed due to the existence of a defect structure of TiO_2 , the Pd atoms existing in the catalyst playing also an important role. In this case, a reversible form of a nonstoichiometric oxide is obtained.

The site conservation equation in terms of fractional coverage is:

$$[X] = 1 - [COX] - 2[OXX] - [OX_s] \quad (11)$$

The rank of the system (8) to (10) can be reduced using assumption:²³

$$[OXX] \ll [COX], [OX_s] \text{ and } [OXX] \cong k_2 [X]^2 / k_{-2} \quad (12)$$

The reaction rate constants for oxidation (k_5) and reduction (k_6) of the subsurface site are much smaller compared with the constants of adsorption (k_1, k_2), desorption (k_{-1}, k_{-2}) surface reaction (k_3) and the formation of the subsurface site (k_4). In the

same time the hypothesis of Eigenberger²⁴ imposes additional restrictions²⁵ which allow reducing the rank of the differential equations. These restrictions are:

$$k_2 P_{O_2}, k_{-2} \gg k_3 \gg k_1 P_{CO}, k_{-1}, k_4, k_{-4} \quad (13)$$

By considering the concentration with the form of fractional coverage 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:

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

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

are obtained. In equations (14)-(15) $\tau = k_{-4} t$, $k_1^* = k_1 / k_{-4}$, $k_{-1}^* = k_{-1} / k_{-4}$, $k_{32}^* = k_2 k_3 / k_2 k_{-4}$ and

$$k_4^* = k_4 / k_{-4}.$$

In such a way the system (8)-(10) is reduced to the system (14)-(15) consisting of two autonomous ordinary differential equations a cubic, equation (14) and a linear one (15).

All the variables of equations (14) and (15) have a physical meaning as long as they are not negative in the region R where they have been studied and $R\{x, z; x_0, z_0 \geq 0; x+z \leq 1\}$ with $x=[COX]$, $z=[X_s]$ and $[X]=1-x-z$.

The steady state for the system eqs (14) and (15) can be obtained by solving a reduced cubic equation as a result of the substitution of equation (15) into equation (14), both in homogeneous term and changing the variable x by:

$$x = y - 2/3 \quad (16)$$

The final equation is:

$$y^3 - py - q = 0 \quad (17)$$

where the coefficients p and q are different functions of k_1^* , k_{-1}^* , k_{32}^* and k_4^* as presented else where.²⁵⁻²⁸

Solving this reduced cubic equation (17) a lot of behaviors where obtained stable solutions, regular or oscillations, stable mode, focus or saddle points.^{25,26}

The reduced cubic equation (17) represents unstable behavior not only in cases with two or three reactants²⁵⁻³⁰ but also in the presence of subsurface oxygen²⁵ or on a non-reactive adsorbed

species.³¹ The oxidation of hydrocarbons of CO produce carbon atoms which remain adsorbed on the surface and can produce oscillations.^{1,32}

The model was used for explaining the oscillations appeared in the Pd/TiO₂ system.

EXPERIMENTAL

A Pd/TiO₂ sample was used. 1% wt Pd supported sample was prepared by impregnation of the TiO₂ (DT51, commercial) support with Pd(OAc)₂ dissolved in acetone. The material was treated at 500°C for 4 hours, after it was dried at 120°C. The sample has a specific surface of 90 m²/g.

The electrical conductance $G=1/R$ where R is the resistance was measured on sample powder (1.5 cm³, fraction between 0.25-0.5 mm) with a precision RLC bridge (Hioki 3532-50 LCR HiTester) which gives directly the parallel electrical conductance G at the fixed frequency of 1592 Hz. At frequency of the measurements the electrical conductivity of the powder is dominated by surface conduction.³³ The sample was flushed in CO:O₂ (1:1 molar ratio) mixture at a temperature of 63°C. The total flow rate was 72 mL/min.

RESULTS AND DISCUSSION

The obtained oscillations of the electrical conductance are presented in Figure 1 at the temperature of about 60°C. As it can be observed, these are nearly irregular oscillations.³⁴

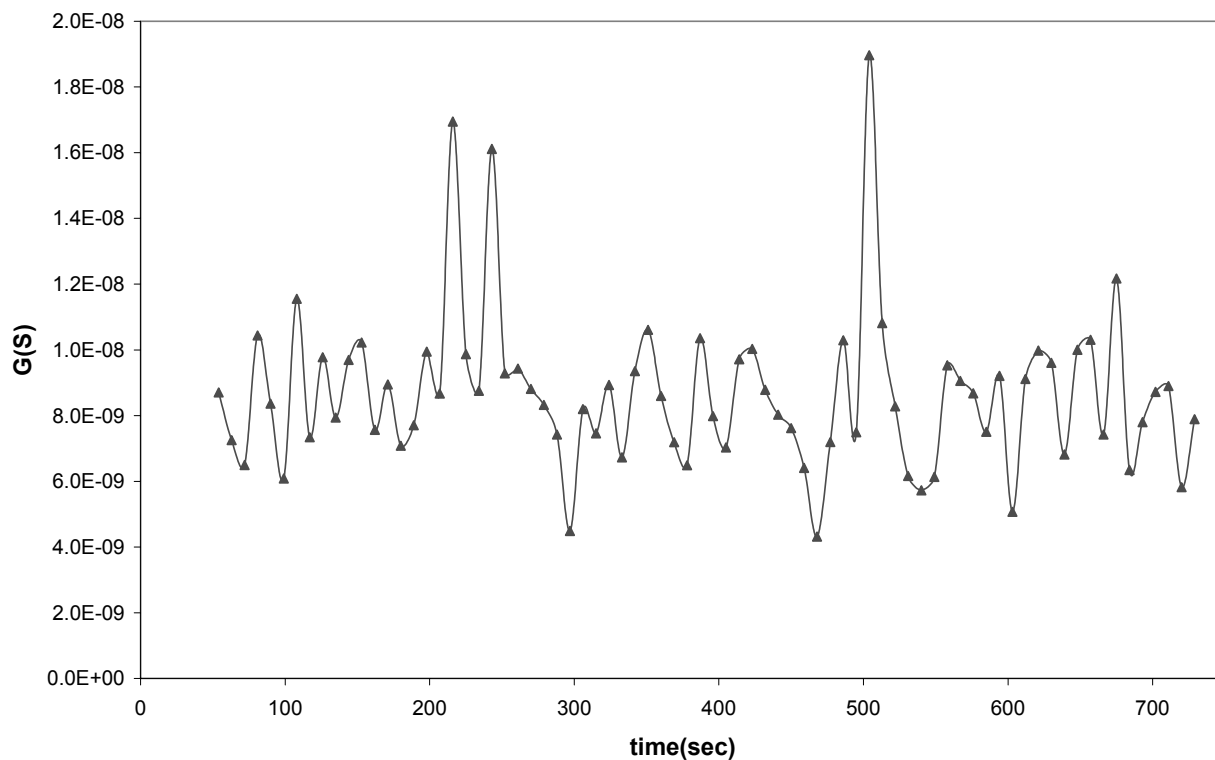


Fig. 1 – Oscillations of the electrical conductance of the Pd/TiO₂ flushed in CO:O₂ atmosphere, at 63°C.

The presence of Pd particles with a narrow distribution on the TiO₂ matrix around 9nm cannot be neglected with oxidation-reduction processes leading to the CO₂ formation.^{7,10,35,36} The obtained nearly isothermal oscillations could be produced by various part of the catalyst with similar properties but at various initial degrees of oxidation or reduction. The coupling of these local oscillators may occur via surface diffusion or diffusion in the gas phase.³⁶ The coupling of Pd clusters via diffusion on the surface of the TiO₂ support cannot be also neglected. Several possible feedback mechanisms have been suggested to describe the experimental data on kinetic oscillations. The mechanism presented in this paper emphasized that the competition of CO and O for the two types of active sites: one on the surface and the other under the surface are responsible for the observed oscillations.

These oscillations can be interpreted as periodic successions of ignited and extinguished states. During the ignition the vacant sites are free and accelerate the reaction, the extinction being connected with the diminution of free sites by their transformation in undersurface sites, with a lower reactivity. This transformation is like a blocking mechanism of the reaction and is reversible.

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 same non-linear processes take place on a local scale but are not visible to the observations, since the seemingly trivial case of stationary state is observed.

CONCLUSIONS

An overall kinetic model and the corresponding mathematical one are presented to explain the oscillations obtained in the Pd/TiO₂ system. The model is based on two types of free sites: one on the surface and the second under the surface. The obtained results are discussed.

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REFERENCES

- N.I. Ionescu and C. Hornoiu, in "Form and Patterns" C. Vasilescu, M.-L. Flonta and I. Craciun (Eds.), Roumanian Academy Printing House, 2015, p. 166.
- G. Ertl, *Adv. Catal.*, **1990**, *37*, 213.
- M.G. Slinko and M.M. Slinko, *Catal. Rev. Sci. Eng.*, **1978**, *17*, 119.
- L.F. Razon and R.A. Schmidt, *Catal. Rev. Sci. Eng.*, **1986**, *28*, 89.
- F. Schüth, B.E. Henry and L.D. Schmidt, *Adv. Catal.*, **1993**, *39*, 51.
- M.M. Slinko and N.I. Jaeger, "Oscillatory Heterogeneous Catalytic Systems, Studies in Surface Science and Catalysis", Elsevier, 1994, vol. 86.
- R. Imbihl and G. Ertl, *Chem. Rev.*, **1995**, *95*, 697.
- H.H. Rotermund, *Surf. Sci. Rep.*, **1995**, *29*, 265.
- C.A. de Wolf and B.E. Nieuwenhuys, *Catal. Today*, **2001**, *70*, 287.
- V.V. Gorodetskii, V.I. Elokhin, J.W. Baker and B.E. Nieuwenhuys, *Catal. Today*, **2005**, *105*, 183.
- N.I. Ionescu, N.I. Jaeger, P.J. Plath and M.A. Liauw, *J. Therm. Anal. Cal.*, **2000**, *614*, 995.
- N.I. Ionescu, N.I. Jaeger, P.J. Plath, M.A. Liauw and C. Hornoiu, *J. Therm. Anal. Cal.*, **2003**, *73*, 851.
- N.I. Ionescu, M. Caldararu, C. Hornoiu and C. Munteanu, *Rev. Roum. Chim.*, **2005**, *50*, 985.
- N.I. Ionescu, M. Caldararu, C. Hornoiu and C. Munteanu, *React. Kinet. Catal. Lett.*, **2007**, *91*, 257.
- N.I. Ionescu, N.I. Jaeger, P.J. Plath, M.A. Liauw and C. Hornoiu, *J. Therm. Anal. Cal.*, **2008**, *91*, 381.
- N.I. Ionescu, N.I. Jaeger, P.J. Plath, M.A. Liauw and C. Hornoiu, *Rev. Roum. Chim.*, **2010**, *55*, 365.
- S. Royer and D. Duprez, *Chem. Cat. Chem.*, **2011**, *3*, 24.
- V.P. Santos, S.S.C. Carabineiro, P.B. Tavares, M.F.R. Ferreira, J.J.M. Orafaio and J.L. Figueiredo, *Appl. Catal. B: Env.*, **2010**, *99*, 198.
- O. Carp, C.L. Huisman and A. Reller, *Progr. Solid State Chem.*, **2004**, *32*, 33.
- T. Garcia, B. Solsona, D.M. Murphy, K.L. Antcliff and S.H. Taylor, *J. Catal.*, **2005**, *229*, 1.
- K. Okumura, T. Kobayashi, H. Tanaka and M. Niwa, *Appl. Catal. B*, **2003**, *44*, 325-331.
- E.U. Franck, *Ber. Bunsenges Phys. Chem.*, **1980**, *84*, 334.
- T. Danciu and N.I. Ionescu, *React. Kinet. Catal. Lett.*, **1992**, *47*, 105.
- G. Eigenberger, *Chem. Eng. Sci.*, **1978**, *33*, 1263.
- N.I. Ionescu, *Rev. Roum. Chim.*, **2010**, *55*, 349.
- N.I. Ionescu and T. Danciu, *Rev. Roum. Chim.*, **1993**, *38*, 783.
- N.I. Ionescu and T. Danciu, *React. Kinet. Catal. Lett.*, **1995**, *54*, 121.
- N.I. Ionescu and T. Danciu, *Rev. Roum. Chim.*, **1999**, *44*, 181.
- T. Danciu, N.I. Ionescu and E.I. Segal, *Rev. Roum. Chim.*, **1997**, *42*, 455.
- N.I. Ionescu, *Rev. Roum. Chim.*, **2009**, *54*, 339.
- N.I. Ionescu, *Rev. Roum. Chim.*, **2011**, *56*, 853.
- N.I. Ionescu, *Rev. Roum. Chim.*, **2012**, *57*, 629.
- M. Caldararu, M. Scurtu, C. Hornoiu, C. Munteanu, T. Blasco and J.M. López Nieto, *Catal. Today*, **2010**, *155*, 311.
- V. Bratan and N.I. Ionescu, *Rev. Roum. Chim.*, **2016**, *61*, 665.
- N.I. Jaeger, M.A. Liauw and P.J. Plath, *J. Chem. Phys.*, **1996**, *104*, 6375.
- M.S. Slinko, E.S. Kurkina, M.A. Liauw and N.I. Jaeger, *J. Chem. Phys.*, **1999**, *111*, 8105.