

*Dedicated to Professor Claude Nicolau
on the occasion of his 80th anniversary*

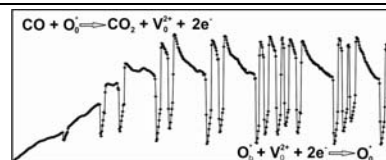
OSCILLATIONS IN THE SYSTEM CARBON MONOXIDE-TiO₂

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Oscillations of the surface electrical conductance of TiO₂ in the presence of CO at 400°C were obtained. These could be explained by a Mars van Krevelen type of mechanism with the difference that in the second step of the reaction the superficial oxygen vacancies are filled with oxygen from the bulk.



INTRODUCTION

When heterogeneously catalyzed reactions are far from thermodynamic equilibrium, new phenomena may develop such as instabilities, oscillations, chemical waves or chaos.¹ The investigation of the dynamic aspects of heterogeneous catalysis has yielded deep insight into details of these reactions on a microscopic level as well as into the complexity of real reaction-diffusion systems. In the same time these oscillatory phenomena in catalytic reactions can be used to perform these processes more efficiently.

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 atmosphere. The main solution was its removing from air by oxidation. Therefore, many studies have been focused on the CO oxidation over metal oxides catalysts.^{2,3}

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.⁴

The goal of this paper is to present the oscillations of the electrical conductivity of the sample surface obtained during the interaction of CO with TiO₂ surface.

EXPERIMENTAL

A commercial TiO₂ (anatase) powder (Rhone-Poulenc) was used.

The surface area of the sample was analyzed using a Micromeritics ASAP 2020 physisorption analyzer using N₂-BET adsorption.

The XRD analysis was performed on a Philips PW 1840 with Cu target and Ni filter (CuK_α λ=1.5418 Å) with 2θ=20-80°.

The diffuse reflectance UV-Vis spectra was recorded by using a Perkin Elmer Lambda 35 equipped with an integrating sphere. The measurements were carried out in the range 800-200 nm, using spectralon as a reference. The obtained data were converted using the Kubelka-Munk function, F(R_∞). The band gap energy was calculated using Tauc method. The linear region of the rising part of the curve ((F(R_∞)-hv)^{1/2} vs hv was extrapolated to zero to get the indirect band gap.⁵

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The electrical conductance $G=1/R$ where R is the resistance was measured on sample powder (1.1 cm^3 , fraction between 0.25-0.5 mm) under the influence of the gas/temperature with a permanent monitoring of the composition of inlet/exit gas using online chromatography. The used cell was a special one described elsewhere.^{6,7} The used cell was connected 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.⁸ The flow rates of research grade CO (5% CO in He) and inert (He) was 5.7 L/h.

The sample was pre-heated in He flow until 400°C and maintained at this temperature 30 min in order to clean the surface.⁹

RESULTS AND DISCUSSION

The sample used has a specific surface of $103 \text{ m}^2/\text{g}$ and consists of 100% anatase with a primary crystallite size measured by XRD at about 16.5 nm and an indirect band gap of 3.2 eV, according with the theoretical value for anatase.¹⁰

The surface conductivity of an oxide is sensitive to the presence of chemisorbed species and to the structural changes. Thus, valuable information about the changes of the catalyst surface produced due to its interaction with environmental atmosphere can be obtained by electrical properties measurements performed in operando conditions.^{7,11-13}

The oscillations of the electrical conductance that appear at 400°C in the studied system are presented in Fig. 1. Under this temperature the evolution of G is a normal one. As could be seen, an induction period is presented after the introduction of CO. At the beginning only one oscillation appears but in time the oscillations become quite regular. The difference between the maximum and minimum of oscillations are quite the same in all cases excluding the first ones. Between the maximum of an oscillation and the beginning of another one there is the same difference in the G value after a certain delay in time. Between the minimum values of G of one series of oscillations and the first oscillation from the next group there is a delay time equal for all regular oscillations.

In addition the concentration of the obtained CO_2 was monitored and presented also in Fig. 1. It could be observed that the concentration of CO_2 is the same and very small during the experiment. The exception was the moment when CO was introduced, when the concentration of CO_2 released is higher due probably to the oxygen not

removed from the surface during the pre-heated period of the sample.

The introduction of oxygen in the system leads to the elimination of oscillations because the system is brought outside the oscillations range.

When a group of oscillations is finished, during the interaction of CO with TiO_2 until a new series begins, a decrease of G is observed, presented in Fig. 2. This decrease obeys an exponential equation for all groups of oscillations. The equation is:

$$G = a + b \exp(-kt) \quad (1)$$

where a , b are constants and t – the time in seconds.

TiO_2 is an n-type semiconductor with a defect structure of the material. In this case the conductivity σ can be expressed as:

$$\sigma = ne\mu = n_0 \left[\exp\left(-\frac{E}{kT}\right) \right] e\mu \quad (2)$$

where n is the number of electrons, E – activation energy of conduction, e - the electric charge of an electron and μ - the mobility of electrons. Because the experiment is performed at a constant temperature μ is constant. For the maximum value of the conductivity, σ_1 , of an oscillation one can write:

$$\sigma_1 = n_1 e\mu \quad (3)$$

and for the minimum value, σ_2 :

$$\sigma_2 = n_2 e\mu \quad (4)$$

Then, the ratio σ_1/σ_2 is:

$$\frac{\sigma_1}{\sigma_2} = \frac{n_1}{n_2} = \exp\left[-\frac{(E_2 - E_1)}{kT}\right], \quad (5)$$

where $(E_2 - E_1)$ represents the difference in activation energy of the upper part of the oscillation to the lower one.

For the whole oscillations $(E_1 - E_2)$ was 0.068 eV and for the upper part where the decrease of σ was an exponential one this value was 0.018 eV. The first value is close to 0.1 eV, the energy of physisorption of CO.

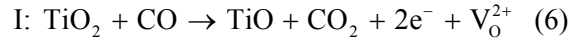
For an entire oscillation the ratio n_1/n_2 was 3.25 and for the oscillation at the beginning of each series was 1.36. The difference between them was about 2. This value could be an indication that in the process two electrons are involved.

The electrical behavior of semiconductors is controlled by various species of chemisorbed

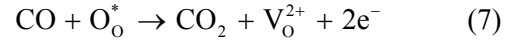
oxygen and the defect chemistry of the oxide. In the case of an n-type semiconductor oxide such TiO₂, an increase in electrical conductance is produced by the increase in the concentration of conduction electrons.

The interaction of the adsorbed CO with TiO₂ surface oxygen with a consequent reduction of Ti⁴⁺ to Ti²⁺ and formation of double ionized vacancies V_O²⁺¹⁴ is proposed in two steps.

In the first step CO reacts with the surface of TiO₂, according to:



or



where O_O^{*} is a superficial oxygen. In this case an increase of electrical conductance is obtained.

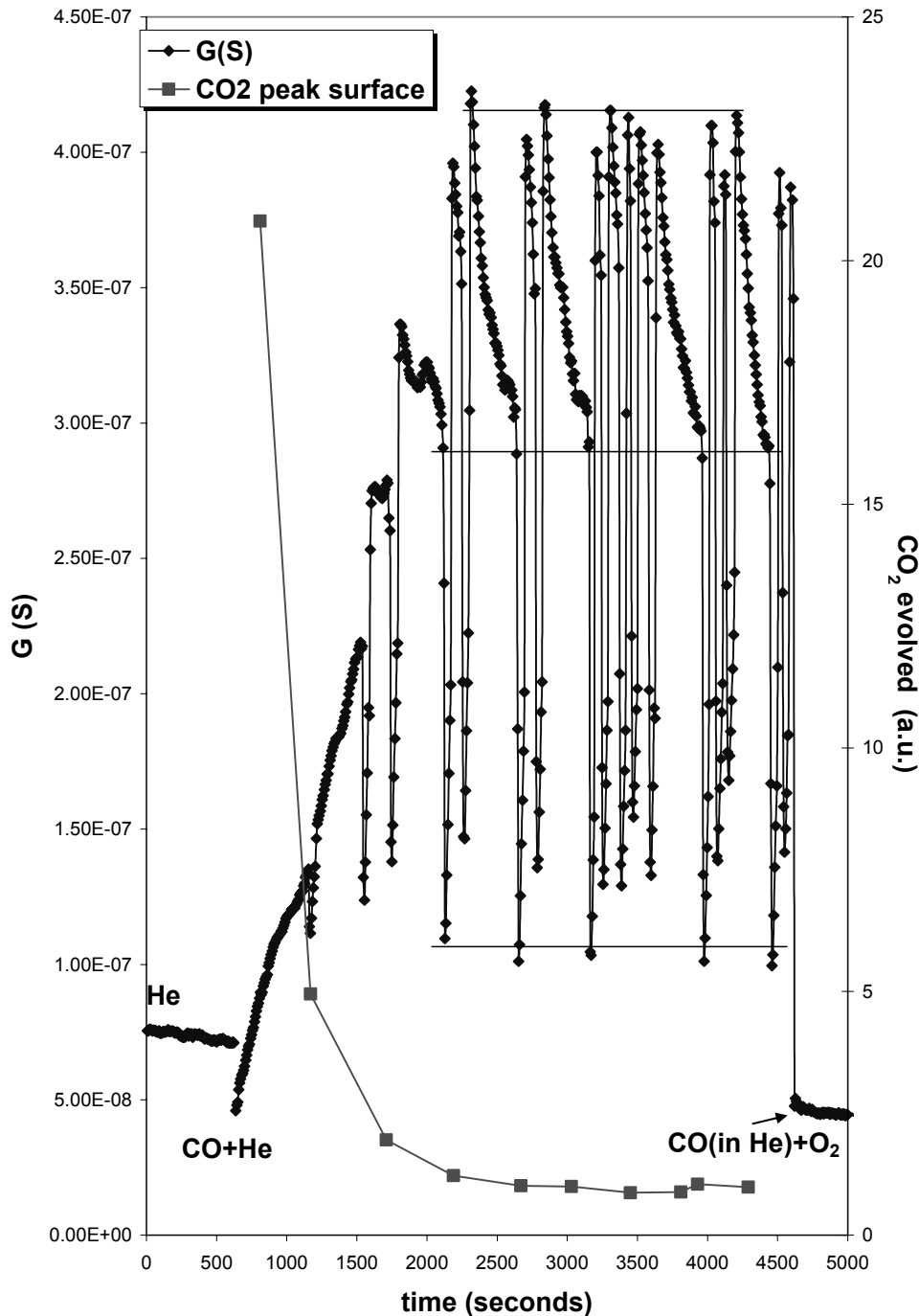


Fig. 1 – Oscillations of the electrical conductance of the TiO₂ surface after the interaction with He, CO in helium and respectively CO (in He)-O₂ mixture.

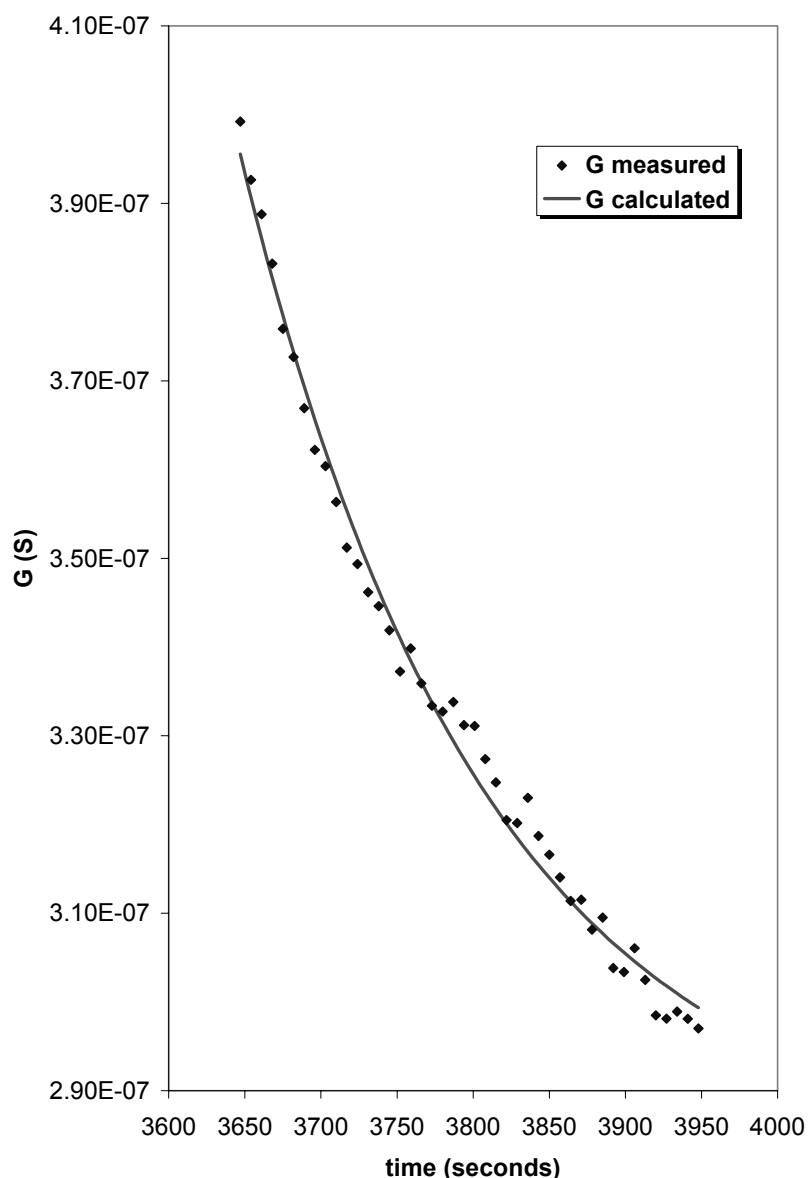
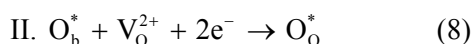


Fig. 2 – Variation of conductivity corresponding to the beginning of an oscillation.

In step II the superficial V_o^{2+} vacancies are filled with oxygen which diffuses through the polycrystalline material with a quasi-constant rate because the concentration of the obtained CO_2 is the same during the experiment. The reaction could be written:



where O_b^* is an oxygen from the bulk of the material.

As a result of this step a decrease of the electrical conductance is obtained.

At the beginning of the second step the rate limiting step is a diffusion represented by:

$$G = \exp\left(\frac{-\pi Dt}{4x_0}\right) = \exp(-k_d t) \quad (9)$$

where D is the oxygen diffusion coefficient in the x direction, x_0 the thickness of the conductivity material and k_d a coefficient characteristic for the oxygen diffusion.¹⁵ The equation (8) is verified when the surface has no sufficient oxygen species. The decrease of the conductivity at the beginning of an oscillation can be represented by equations (9) and is represented in Fig. 2.

This type of mechanism is a kind of Mars van Krevelen type¹⁶ with the difference that in the second step the surface is fed with oxygen not from the gas phase but from the bulk of the

material. The Mars van Krevelen type of oxidation can present two possibilities for the second reaction step. The lack of surface oxygen can be compensated either by oxygen from the gas phase or by oxygen from the bulk of the oxide. The introduction of oxygen in gas mixture produces a steep modification of the reaction conditions. Oxygen is quickly adsorbed on the TiO₂ surface and the oscillations disappear.

The electrical conductivity is a very sensitive method to detect oscillations which cannot be observed by an usual analytical method. This could be also an explanation that the detection of oscillatory reaction is quite difficult and many oxidation reactions, which could be oscillatory ones, are considered to present a normal behavior.

Any realistic system requires, in principal, a large number of variables for its full description, but, due to a separation of time and length scales, only a few of these many degrees of freedom are really important for the dynamics of the system.^{17,18} To model the oscillations, two essential aspects have to be taken in consideration on the microscopic level to find the smallest unit, which is capable to oscillate and on the macroscopic level to find the global synchronization mechanism which produces macroscopic variation of the investigated parameter. The more general case is that of same non-linear processes which take place on a local scale but not-visible to observation, since the seemingly trivial case of stationary step is observed.

CONCLUSIONS

Oscillations of the electrical conductance have been observed in the system CO/TiO₂. The oscillation of TiO₂ surface electrical conductance after the interaction with CO could be explained by a kind of Mars van Krevelen type with the

difference that in the second step of the reaction the surface is fed with the oxygen which diffuses from the bulk of the material.

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