OXYGEN PARTIAL PRESSURE DEPENDENCE OF ELECTRICAL CONDUCTIVITY ON TiO₂ AND Pd/TiO₂

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The electrical conductivity of n-type TiO₂ and Pd/TiO₂ samples has been determined as a function of oxygen partial pressure and temperature. In case of TiO₂, the defect chemistry reveals at 400°C the existence of neutral oxygen vacancies. In case of Pd/TiO₂ at 400°C the major defect seems to be the singly ionized oxygen vacancies. The results have been discussed.

INTRODUCTION

Titania (TiO₂) is a widely studied transition metal oxide material. The main motivation for studying titania comes not from its use as a gas sensing material, but rather because its importance as a photocatalyst.[1]

The gas response to oxidizing or reducing gases can be detected by measuring the conductivity of metal oxide material. The change in the conductivity upon exposure to gases may have two different contributions: i) a change of the bulk charge carrier concentration due to the formation or annihilations of intrinsic dopants by reduction and oxidation of the gas; ii) a surface band bending induced by chemisorbed or ionosorbed charged surface species[2] or the reaction of gas molecules with such adsorbed species. The surface band bending induces shift of the energy level relative to the Fermi level and as a result one obtains a change of the charge carrier population. In addition it also induces barriers at grain boundaries that influence the charge transport.[1]

For TiO₂ some informations reveal that the electronic structure of the bulk material and nearly perfect surfaces cannot be distinguished and that the radiation induces predominantly oxygen vacancy point defects in the uppermost surface layer.[2, 3] The conductivity changes are obtained due to the variation of dopants as a consequence of formation of oxygen vacancies and Ti interstitials. The relationship:

$$\sigma \propto p_{O_2}^n$$

where σ is the conductivity, $p_{O_2}^n$ the pressure of oxygen and n a sensitive exponent to the predominating point defect, yields a first information about the defect structure of the material.[4]

To increase the activity/selectivity of metal oxide catalyst, a variety of different additives can be used. These additives act either as dopants in the metal oxide bulk or reside at the surface in the form of clusters. Surface clusters are commonly differentiated into chemical and electronic sensitizers. Chemical sensitizers act mainly as heterogeneous catalysts. Electronic activation is

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due to a change of Schottky barrier at the interface between a supported cluster or metallic atoms and the semiconducting metal oxide material. This is the case of transition metal additives such as Pd[4] in case of oxidation or reduction reactions reflected in the topography of inter-grain areas and thus in the height of inter-grain Schottky-type barriers. The increase of the Schottky barrier at the interface of the solid-gas system produces a band bending in the material and consequently a change in the conductivity of the system.

The goal of this paper is to study the influence of oxygen partial pressure and temperature on the electrical conductivity of TiO_2 and Pd/TiO_2 in order to determine the major oxygen or metal defects involved in the electrical conductivity of the samples.

RESULTS AND DISCUSSION

Model conduction in TiO₂ and Pd/TiO₂

Let Me^{n+}, with $n \geq 1$, the metal existing in an oxide semiconductor. The defect chemistry of such an oxide is determined by the equilibrium between neutral V_O^* or charged oxygen vacancies V_O^+ and V_O^{2+}, lattice oxygen O_O^*, conduction electrons e^-, ionized Me interstitials and oxygen in the gas phase. The interaction of lattice oxygen with gaseous atmosphere can be described, with a Frenkel point defect structure by the reaction:

$$O_o^* \xleftrightarrow{K_1} V_O^* + \tfrac{1}{2} O_{2(g)} \qquad (1)$$
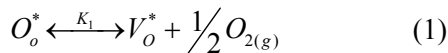
followed by the subsequent ionization reactions:

$$V_O^* \xleftrightarrow{K_2} V_O^+ + e^- \qquad (2)$$

$$V_O^+ \xleftrightarrow{K_3} V_O^{2+} + e^- \qquad (3)$$
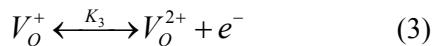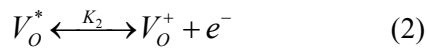
where K_1, K_2 and K_3 represent equilibrium constants and V_O^+ and V_O^{2+} are singly or doubly ionized oxygen vacancies respectively.

The electroneutrality condition requires that:

$$[e^-] = [V_O^+] + 2[V_O^{2+}] \qquad (4)$$

Substitution of V_O^+ and V_O^{2+} with the aid of K_1 - K_3 constants yields to:

$$[e^-] = (K_1 K_2)^{\frac{1}{3}} p_{O_2}^{-\frac{1}{6}} ([e^-] + 2K_3)^{\frac{1}{3}} \qquad (5)$$

There are now several cases:

a) if V_O^{2+} dominate, i.e. $2K_3 \gg [e^-]$, then equation (5) becomes:
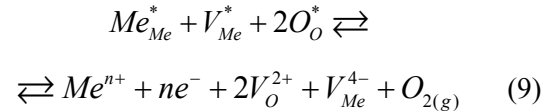
$$[e^-] = (2K_1 K_2 K_3)^{\frac{1}{3}} p_{O_2}^{-\frac{1}{6}} \qquad (6)$$

b) if V_O^+ dominate, i.e. $2K_3 \ll [e^-]$, then equation (5) has the form:

$$[e^-] = (K_1 K_2)^{\frac{1}{2}} p_{O_2}^{-\frac{1}{4}} \qquad (7)$$

c) if V_O^* is the principal defect, then:

$$[V_O^*] = K_1 p_{O_2}^{-\frac{1}{2}} \qquad (8)$$

If n=4 then a Me_{Me}^* vacancy may be form according to the reaction:

$$Me_{Me}^* + V_{Me}^* + 2O_O^* \rightleftarrows$$

$$\rightleftarrows Me^{n+} + ne^- + 2V_O^{2+} + V_{Me}^{4-} + O_{2(g)} \qquad (9)$$

where V_{Me} is a Me vacancy.

$$\text{If } n[e^-] \gg 2[V_O^{2+}] \gg [V_{Me}^{4-}] \qquad (10)$$

then

$$[Me^{n+}][e^-]^n = K_n p_{O_2}^{-1} \qquad (11)$$

Because of electroneutrality:

$$[e^-] = [Me^{n+}] \qquad (12)$$

and finally:

$$[e^-] \propto p_{O_2}^{-\frac{1}{n+1}} \qquad (13)$$

When the metal is titanium fully oxidized Ti^{4+} then a dependence $p_{O_2}^{-\frac{1}{5}}$ can be obtained. The exponents *n* can vary between 1 and 4 and several dependencies between the concentration of electrons and the pressure of oxygen may be obtained.

In the system Pd/TiO_2 where the concentration of Pd was 1% - doped equivalent, about 0.9 from this 1% Pd has been found on the surface of titania by XPS-spectra.[10] In these conditions Pd acts on a TiO_2 surface and the following equilibrium can be obtained:

$$4PdO + TiO_2 \longleftrightarrow 4Pd_{Ti}^+ + V_{Ti}^{4-} + 6O_o^* \qquad (14)$$
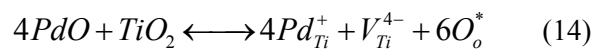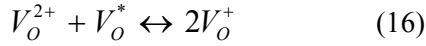
In the high temperature range of the working temperature the surface Pd clusters becomes progressively oxidized to PdO.[11-15]

The formation of PdO could be explained by the reaction between the lattice oxygen of TiO₂ namely O_O^* and Pd according to:

$$Pd + O_O^* \leftrightarrow PdO + V_O^{2+} \qquad (15)$$

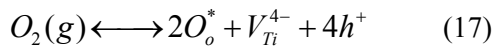followed by

$$V_O^{2+} + V_O^* \leftrightarrow 2V_O^+ \qquad (16)$$
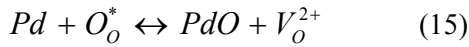
The addition of Pd increases the concentration of double or monoionized vacancies.

The lattice oxygen O_o^* resulted conform equation (14) can be involved in reactions with oxygen from the gas phase according to:

$$O_2(g) \longleftrightarrow 2O_o^* + V_{Ti}^{4-} + 4h^+ \qquad (17)$$

But the electroneutrality condition demands that:

$$[V_{Ti}^{4-}] = 4[Pd_{Ti}^+] \qquad (18)$$

and

$$[e^-][h^+] = K \qquad (19)$$

Using now equations (18) and (19) in relationship (17) one obtains finally:

$$[e^-]\alpha[Pd_{Ti}^+]^{1/4} P_{O_2}^{-1/4} \qquad (20)$$

Results

The experimental results are presented in Figs. 1, 2 and 3.

In Fig. 1 are given the UV-Vis spectra of both TiO₂ and 1% Pd/TiO₂ samples. A broad band between 400-500 nm centered at 470 nm could be observed in the absorption spectra of Pd/TiO₂, owing to d-d transition of PdO particles.[16,17] The spectra displays a characteristic absorption edge around 375 nm for TiO₂ and 380 nm for Pd-doped equivalent, corresponding to a band gap of 3.3eV and 3.2 eV respectively, in according with theoretical value for anatase (3.2 eV).[18]

Figs. 2 and 3 present the conductivity of TiO₂ and Pd/TiO₂ samples respectively as a function of oxygen partial pressure at temperatures between 300 and 430°C. Between these temperatures an increase of conductivity is observed with diminishing p_{O_2} for both samples, characteristic for the n-type semiconductors.
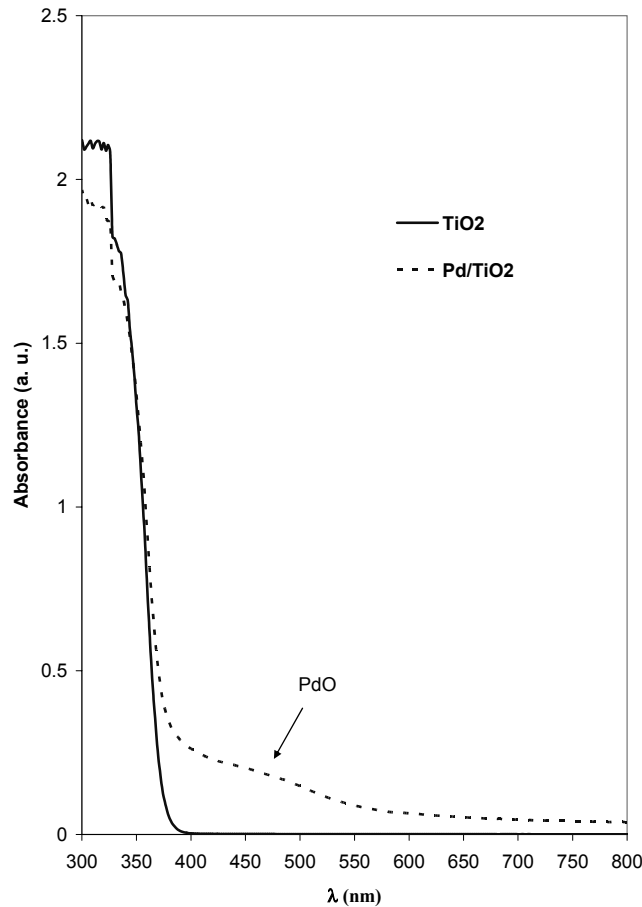

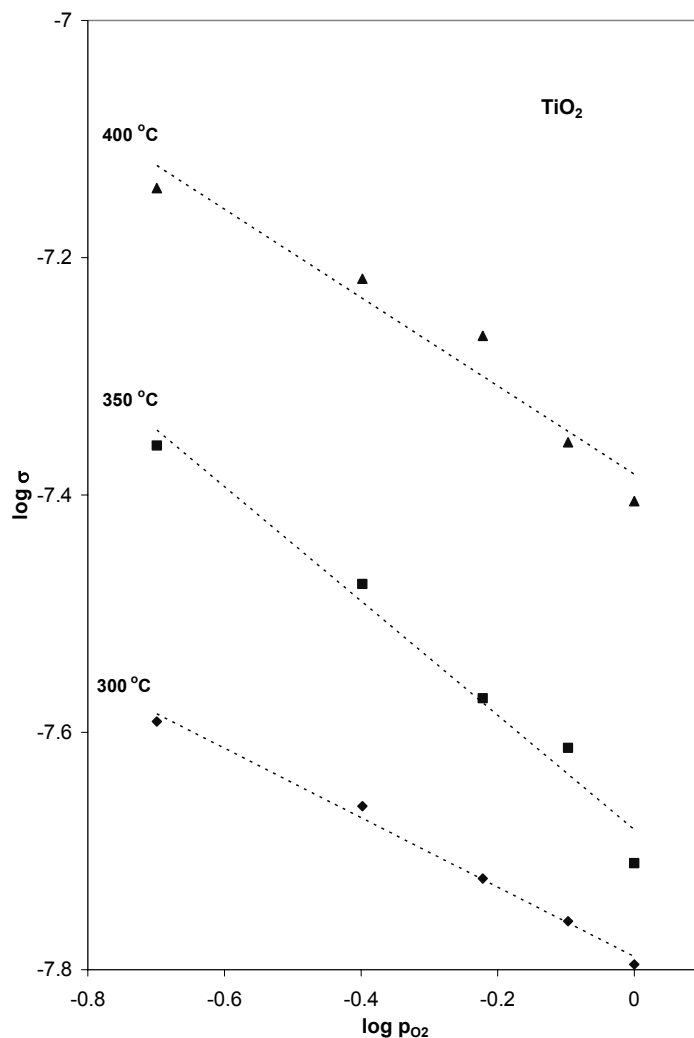Fig. 1 – UV-Vis spectra of TiO₂ and Pd/TiO₂.

Fig. 2 – Dependence of oxygen partial pressure (expressed in atm)
of electrical conductivity (S/m) in TiO$_2$ at different temperatures.

Up to 200ºC the concentration of holes is equal to that of electrons and the conductivity of both samples are invariant with changes of oxygen partial pressure. At 250ºC one observe a small influence of the partial pressure of oxygen on the TiO$_2$ sample which becomes visible between 300 and 400ºC. For the Pd/TiO$_2$ sample this influence became visible from 350ºC to 430ºC.

The value of the exponent n is obtained from equation (1) used in the form:

$$\log \sigma = \alpha + n \log p_{O_2} \qquad (21)$$

where α is a constant.

The calculated value for the exponent n for both samples are presented in Table 1.

Discussion

For TiO$_2$ sample the observed value at 250ºC can be explained in the same way as for the temperature of 200ºC: concentration of electrons and holes quite equal. At 300ºC the value obtained is close to $-1/4$ indicating, according to equation (7), a domination of V_O^+ vacancies. At 350 and 400ºC the obtained value is close to $-1/2$, in this temperature range V_O^* being the dominant specie according to equation (8). This V_O^* specie can appear due to a loss of oxygen from TiO$_2$ at the working temperature.

In the same time, oxygen partial pressure dependencies with slopes of $-1/2$ and $-1/4$ would indicate single and trivalent titanium interstitials Ti$^+$ and Ti^{+3} respectively, according to equation (13). These defects can appear if the electrons are trapped at cations.[4] Such donor-type defects seems to be improbably because the sample are pure without a dopant.
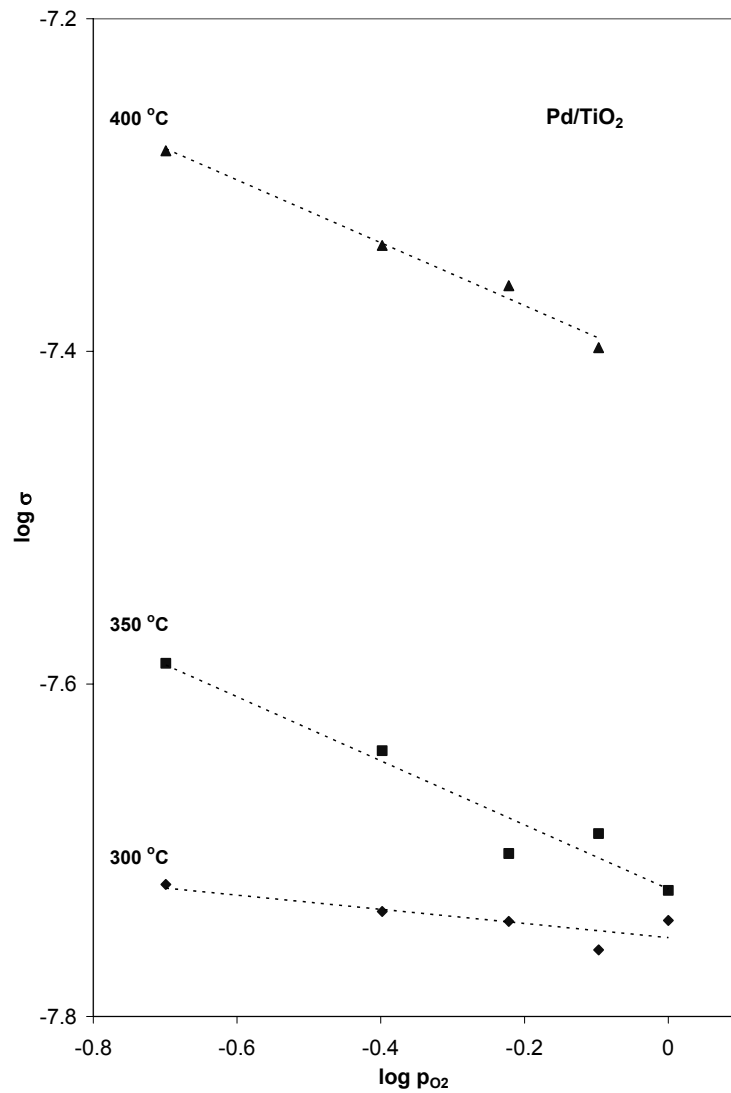
Fig. 3 – Dependence of oxygen partial pressure (expressed in atm)
of electrical conductivity (S/m) in Pd/TiO$_2$ at different temperatures.

Table 1

Determination of the exponent n for TiO$_2$ and Pd/TiO$_2$ samples

Temperature (ºC)	n for TiO$_2$	n for Pd/TiO$_2$
250ºC	-0,05	-
300ºC	-0,29	-0,04
350ºC	-0,48	-0,19
400ºC	-0,48	-0,19
430ºC	-	-0.15

The presence of Pd on the TiO$_2$ surface produces changes in the conductivity behaviour. The sample becomes more stable because only at 300ºC one observes a small change in the conductivity.

At 350ºC and 400ºC the conductivity values are quite the same and this behaviour leads to a value closer to $-1/4$ for the exponent n, being explained according to equation (6) by the vacancies V_O^+ introduced by Pd on the surface (equations (15)-(16)). At 430ºC the value of n seems to be closer to $-1/6$, conformly to equation (7): This last value is obtained when V_O^{2+} dominate the conduction. It seems to be very difficult to make a clear distinction between these values. More probable is that both vacancies contribute to the electronic conduction. These obtained results

demonstrate that the electrical properties of the system is strongly influenced by the surface behaviour of the PdO_x supported phase. This in turn are reflected in the sensitivity of inter-grain Schottky barriers to the environmental factor and consequently in the observed electrical characteristic of the surface in the presence of oxygen.

The interaction of oxygen with a vacancy containing TiO_2 surface[4] investigated by electron energy loss (EELS)[19] and temperature programmed desorption (TPD)[20] has indicated that O_2 adsorbs and dissociates at surface O-vacancies. The results have suggested that one oxygen atom heals the surface defect and the other O-atom is adsorbed on the Ti. No molecular O_2 adsorption down to 100K was found on a defect free surface.[1]

In case of Pd/TiO_2 it seems very likely that Pd is oxidized by oxygen with the formation of an PdO_x ($0 < x \leq 1$). This oxide increases the Schottky barrier at the grains interface inducing a band bending of the material. This mechanism depends on the interface composition between the clusters of additive and the metal oxide interface.[21]

Stabilization of oxides of late transition metals at oxide interface has been reported for oxidized Pd clusters on Fe_2O_3 substrates.[22] This suggests that formation of a higher oxidized interface may be a general phenomenon for oxidized late transition metal clusters supported on metal oxide supports.[4] In case of Pd on Fe_2O_3 it was suggested that this interface oxide acts as an oxygen reservoir for catalytic oxidation reactions. A change of the interface oxygen concentration can produce a gas response due to variations in the Schottky barrier between the clusters and the support.

EXPERIMENTAL

For measurements two samples were used: a commercial TiO_2 (anatase) powder (Rhone-Poulenc) and its 1%Pd-doped equivalent, obtained by impregnating the support with palladium acetate (Aldrich). Palladium solution in acetone was added over the support under stirring, than the impregnated powder was heated at 80^oC until completely dried. The resulted powder was calcined at 500^oC for 4 hours in air flow.

The electrical conductance (G=1/R, where R is the resistance) was measured on samples powder (1.5 cm^3, fraction between 0.25-0.5 mm) under the influence of the gas/temperature, using a special reaction cell.[6-9] This cell consists in two coaxial tantalum cylinders as electrodes, embedded in a Pyrex glass tube and connected by tungsten wires to a precision RLC bridge (HIOKI 3522-50). The sample was filling the annular space between the electrodes and supported on a frit. The G values were obtained when the system catalyst-gas has attainted its equilibrium. Temperature

in the powder bed was monitored with a thermocouple located in the center of the cell.

The conductivity was evaluated by considering the cell as a cylindrical condenser, with the powder to be measured as the dielectric, by substracting from the measured G value the corresponding value of the empty part.[8]

To reduce the surface of oxides, an initial heating in helium between room temperature and 400^oC (with a ramp of $5^o/min$) was made. Electrical measurements at various temperatures (from 200 to 430^oC) at different oxygen pressure ranges (from 0.2 to 1 atm) were performed. Controlled atmospheres were secured by continuous flow of 72 mL/min of $He-O_2$ mixtures regulated by independent mass flow controllers.

Additional characterization by UV-Vis spectra was performed. Diffuse reflectance UV-Vis spectra were recorded by using a spectrophotometer Perkin Elmer Lambda 35, equipped with an integrating sphere. The measurements were carried out in the range 900-200 nm, using MgO as a reference. The reflectance measurements were converted to absorption spectra using the Kubelka-Munk function, F(R).

CONCLUSIONS

The electrical conductivity of TiO_2 and Pd/TiO_2 samples has been determined as a function of oxygen partial pressure and temperature. At 300^oC singly ionized oxygen vacancies predominate and at 400^oC the neutral oxygen vacancies.

The system $Pd/TiO_2/O_2$ is more stable than TiO_2/O_2 one and at 350^oC or 430^oC one obtains a domination of single or double ionized oxygen vacancies.

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