



ADSORPTION KINETICS IN THE SYSTEM ZnO FINE POWDER/O₂

Nicolae I. IONESCU* and Monica CĂLDĂRARU

Roumanian Academy, "Ilie Murgulescu" Institute of Physical Chemistry, 202 Splaiul Independentei, 060021 Bucharest, Roumania

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The adsorption kinetics of oxygen on ZnO fine powder supported on a metal surface can be described by a mechanism involving an electron transfer from the oxide to the adsorbed oxygen.

INTRODUCTION

The oxygen adsorption on solid surfaces can be often described by a logarithmic rate law¹⁻⁴ used either in its integral form:

$$q = \frac{I}{\beta} [\ln(t + t_0) - \ln t_0] \quad (1)$$

or in its differential one

$$\frac{dq}{dt} = \alpha \exp(-\beta q) \quad (2)$$

where q is the amount of the adsorbed gas at the time t , α , β are constants and $t_0 = \frac{I}{\alpha\beta}$ if for $t=0$, $q=0$.

In our previous papers⁵⁻¹¹ concerning the logarithmic rate law of adsorption in the system ZnO/O₂ we have shown that it can be derived by using models involving the charge transfer from the solid surface to oxygen species.

In the present paper we intend to extend this model to the case of a very fine ZnO powder /O₂ system deposited on a metal surface.

THE MODEL

The present model on the logarithmic rate law in the system ZnO/O₂ is based upon the fact that

the gas/semiconductor contact can be considered as being similar to that existing at the metal/semiconductor oxide junction.^{1,2}

As it is known¹², in temperature ranges up to 200°C the dominant oxygen specie adsorbed on a ZnO surface is O₂⁻ resulting in the reaction:



with the rate equation describing the evolution of oxygen adsorption:

$$\frac{dQ_s}{dt} = \gamma P_{O_2} [e^-] \quad (4)$$

Here Q_s is the surface charge due to oxygen adsorption, $[e^-]$ is the concentration of electrons at the interface ZnO/O₂, P_{O_2} the pressure of oxygen and γ is a constant. The problem is now to find the connection between the charge Q_s and the concentration of electrons $[e^-]$.¹²

Let us consider now a very fine powder of ZnO deposited on a metal surface. We assume that the grains are spheres having a homogeneous size distribution. If the grains have a radius R of 0.1 μm and the space charge layer is as usual 10⁻⁵ – 10⁻⁶ cm it means that each grain consists practically only of the space charge layer.

In the case of oxygen adsorption on a normal ZnO-crystal the usual band bending is between

* Corresponding author: ionescu@chimfiz.icf.ro

0.4 – 0.6 eV. Such band bending values are obtained by adsorption of $2 \cdot 10^{11}/\text{cm}^2$ oxygen species.^{1,2} Because as known 10^{15} sites/ cm^2 are available for adsorption on the oxide surface, this means that only $2 \cdot 10^{-4}$ of all available sites are covered with adsorbed oxygen species¹³.

In the case mentioned above, of a very fine powder (the whole grain consists only of the charge layer) the surface charge Q_- produced by these adsorbed oxygen species must be equal with the charge of c_+ monoionized donors in the bulk of grains, *i.e.*:

$$4\pi R^2 Q_- = \frac{4}{3} \pi R^3 c_+ \quad (5)$$

For a concentration of monoionized donors in the bulk around 10^{16} donors/ cm^3 (and by supposing that all the donors are ionized) one obtains from equation (5):

$$Q_- = \frac{c_+}{3} R \quad (6)$$

which gives the maximum possible value of $3.3 \cdot 10^{10}$ adsorbed oxygen species. The number of adsorbed oxygen species will be small because all the free electrons available from grain will be captured by the adsorbed gas.

This value for the adsorbed oxygen species is smaller with one order of magnitude than that producing the usual band bending on a ZnO crystal and the corresponding band bending will be around $7 \cdot 10^{-2}$ eV,^{1,2} much smaller in comparison with the usual value for ZnO. Thus for very fine powders the band bending is unimportant and can be neglected.

To increase the number of adsorbed oxygen species, which is important in surface reactions it is necessary to increase the number of electrons available on the surface. This can be realized by supporting the powder on a metal, which offers a big reservoir of electrons.

The direction of the charge transfer in the system metal/ZnO in an ideal Schottky barrier model is determined by the relative positions of the Fermi level of the metal and the semiconductor.¹⁴ When the energy of the Fermi level of the metal is higher than that of the semiconductor both materials being into intimate contact, the electrons will flow from the metal to the semiconductor. An electronic equilibrium is established between the metal support and the grains. As a result the Fermi energy has the same value in the whole system oxide powder/metal.

Supplementary electrons arriving on the grain will be uniformly distributed on the surface. The band bending being very small, it can be assumed that the bands remain flat. The surface potential V of the small grains due to the space charge at the oxide/gas oxide contact can be obtained from electrostatics:

$$V = \frac{Q_-}{C} \quad (7)$$

where C is the double layer capacity which depends on the geometry and the dielectric constant of the material. Due to the arrival of new electrons the whole grain potential is increased. The bands remaining flat, this will occur by the increase of the distance between the bottom of the conduction band and the Fermi level and the decrease of the distance between the valence band and the Fermi level.

Coming back to equations (5) and (6) and taking into account that for a sphere the capacity is $C = 4\pi\epsilon R$ (where ϵ is the dielectric constant of ZnO), one obtains in this case:

$$V = \frac{4\pi R^2 Q_-}{4\pi\epsilon R} = \frac{Q_-}{\epsilon} R \quad (8)$$

The dependence of the concentration of electrons on temperature is:

$$[e^-] = A \exp\left(-\frac{eV}{kT}\right) \quad (9)$$

where e is the charge of an electron, k and T have their usual meanings and A is a constant. Using the relationships (8) and (9) one obtains for equation (4):

$$\frac{dQ_-}{dt} = A\gamma P_{O_2} \exp\left(-\frac{eR}{\epsilon kT} Q_-\right) \quad (10)$$

which is nothing else than the differential form of the logarithmic equation (2).

It should be mentioned that usually in order to claim the existence of a logarithmic kinetics for adsorption or desorption processes, it is necessary to fit the data over a large range of experimental values.¹⁵⁻¹⁸

Equation (9) demonstrates that the theory of ionosorption can be successfully used to describe oxygen adsorption in the case of the very fine ZnO powder deposited on a metal surface, when adsorption did not reach saturation.

CONCLUSIONS

The kinetics of oxygen adsorption on ZnO fine powder supported on a metal surface can be

described with a model based on ZnO feeding with electrons provided by the metal support, by taking into account the charge transfer of an electron from the solid surface to the adsorbed oxygen species.

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