DESORPTION KINETICS IN THE ZnO NANOPOWDER / O₂ SYSTEM

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The desorption kinetics of oxygen from ZnO nanopowder supported on a metal surface was analyzed. It was shown that it can be described by a logarithmic rate law, by using a model taking into account the charge transfer from the oxygen adsorbed species to the solid surface.

INTRODUCTION

The oxygen desorption from a solid surface can be often described by a logarithmic rate law [1-4] used either in its differential form:

$$-\frac{dq}{dt} = \alpha \exp(\beta q) \qquad (1)$$

or in its integral one:

$$q = \frac{1}{\beta}\left[ln t_0 - \ln(t + t_0) \right] \qquad (2)$$

where q is the amount of the desorbed gas at the time t, α, β are constants and $t_0 = \frac{1}{\alpha\beta}$ if for $t=0$, $q=0$.

In our previous papers [5-9] concerning the logarithmic rate law followed by the desorption of gases from solid surfaces, particularly in case of desorption of oxygen from a ZnO film deposited on a metal surface we have shown that this rate law can be deduced by using models involving the charge transfer from oxygen species to the solid surface.

In the present paper we intend to extend this model to the case of ZnO nanopowder, *i.e.* for the system O₂/ZnO nanopowder/metal.

THE MODEL

Let us consider a ZnO nanopowder having a homogeneous nanosized distribution of particles deposited on a metal surface.

If the grains have a radius of 0.1μ and the space charge layer is as usual[1] between $10^{-5} - 10^{-6}$ cm, than each grain consists only of space charge layer. In this case the upward bending at the surface of valence respectively conduction bands (usually around 0.4 -0.6 eV on ZnO[1,2]) will be much lower due to the low electron concentration in the space charge layer. When such a ZnO nanopowder is deposited on a support richer in electrons, *e.g.* a metal, the transfer of electrons from the metal to the powder, will occur till the electronic equilibrium between the powder and support is established. The conduction bands, due to the small band bending, have the same energy level and the surface potential would be the same for all particles. The whole powder will have an uniform conduction band resembling that of a semiconductor single crystal.[10]

If some electrons arrive on or leave the surface, this will influence the surface potential of particles, by increasing or decreasing it respectively. From electrostatics is known that the charge Q is connected with the potential V through the relationship:

$$Q = CV \qquad (3)$$

where C is the capacity.

The arriving/leaving electrons can move also easily between grains because the conduction bands of the grains have the same energy. This happens when the equilibrium of the free electrons in the solid is faster than the equilibrium between the adsorbed particles and the free electrons of the solid.

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At the same time, at thermodynamic equilibrium the system nanopowder – metal reaches the same value of the Fermi energy E_F. The adsorption – desorption phenomena occur in all particles in the same manner and the surface potential is the same for all particles.

The area between two particles with space charge layers can be viewed as a condenser and the series of nanoparticles could be considerrd as a series combination of condensators without dielectric.

Let's consider the initial conditions:

$$Q_0 = C V_0 \qquad (3)$$

where Q_0 is the charge and V_0 the surface potential before the start of desorption.

We assume now that the adsorbed oxygen species are in the form of $O_2^-(ads)$ i.e.:

$$O_2^-(ads) \rightarrow O_2(g) + e^- \qquad (4)$$
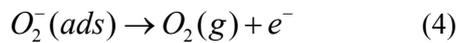
The existence of charged oxygen species on a ZnO surface was demonstrated by ESR spectroscopy [11,12] and ^{17}O isotopic labeling.[13,14]

By heating the system, thermal desorption of oxygen occurs. In these conditions the electrons released by desorbing oxygen species can move back through ZnO to the metallic support (Fig. 1) which brings a decrease of the potential V. The surface charge becomes now:

$$Q = C\,(V_0 - V) \qquad (5)$$

The desorption of the charged oxygen species adsorbed on ZnO surface determines an electrostatic potential difference V at the interface ZnO/O_2 and the concentration of electrons can be expressed by:

$$\left[e^-\right] = k_1 \exp\left(-\frac{eV}{kT}\right) \qquad (6)$$

where k_1 is another constant and k and T have their usual meanings.

Equation (6) is valid if the rate of desorption is slower than the electrons movements in oxide.

From equation (4) one obtaines:

$$-\frac{d\left[O_2^-(ads)\right]}{dt} = k_2 P_{O_2} \left[e^-\right] \qquad (7)$$
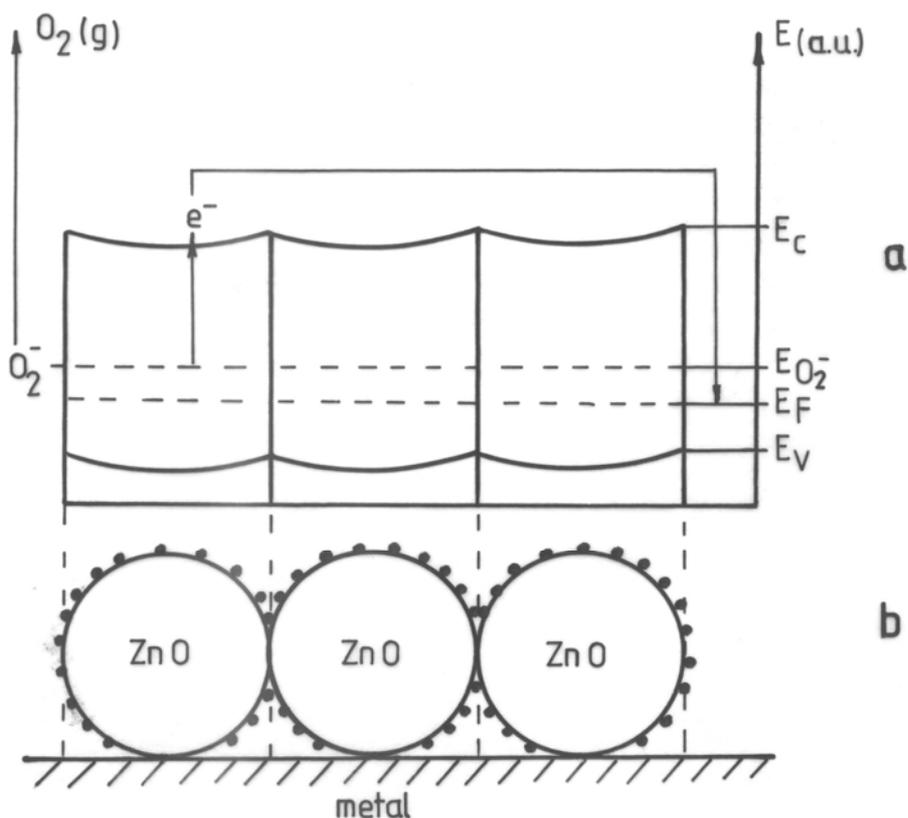

Fig. 1 – Oxygen desorption from ZnO nanoparticles.
a) theoretical model; b) physical model $\bullet = O_2^-(ads)$.

At the same time according to eq. (4) the surface charge is:

$$Q = a\,[\,O_2^-(ads)\,] \qquad (8)$$

and

$$-\frac{dQ}{dt} = bP_{O_2}\left[e^-\right] \qquad (9)$$

where $b = k_2/a$, a and b being constants.

Taking into account the equations (5), (6), (7) and (9) one obtains:

$$-\frac{dQ}{dt} = cP_{O_2}\exp\left[\frac{e}{kT}\left(\frac{Q}{C} - V_0\right)\right] \qquad (10)$$

which is nothing else then the differential form of the logarithmic rate law of desorption and

$$c = \frac{k_1 k_2}{a}$$

The present model of the logarithmic rate law of desorption is based upon the fact that the gas/semiconductor interface is similar to that which exists at the metal/semiconductor junction. In the present model the rate determining step is the desorption of charged oxygen species existing on ZnO particles surface. Very probably, as we pointed out[9] these simple models previously described and the present one are not the only one which explain the occurrence of the logarithmic rate law of desorption. This situation is similar with that existing in the case of the logarithmic rate law of adsorption where we described with many models such a law.[5,15-21] Several possible mechanisms containing relevant elementary steps for adsorption and desorption can exist, but probably only few of them can be regarded as representing a realistic situation. To find either a general mechanism explaining the logarithmic rate law of adsorption and desorption or several

mechanisms for specific gas-solid systems remains an open problem.

CONCLUSIONS

The logarithmic rate law of the oxygen desorption from ZnO nanopowder deposited on a metal surface can be explained by a model involving the charge transfer from the oxygen species to the solid surface.

REFERENCES

1. K. Hauffe and S. R. Morrison, "Adsorption", de Gruyter, Verlag, Berlin, 1974, p.87.
2. S.R. Morrison "The Chemical Physics of Surfaces", Plenum Press, New-York and London, 1978, p. 46, 241.
3. E.I. Segal, N.I. Ionescu, D.M. Razus, I.N. Sălăgeanu, "Cinetica reacţiilor catalitice eterogene", vol I, Ed. Academiei Române, 1992, p. 87.
4. E.I. Segal, C. Iditoiu, N. Doca, D. Fătu, "Cataliză şi Catalizatori". Ed. Facla, Timişoara, 1986, p. 40.
5. N.I. Ionescu and B. Aurian – Blăjeni, *Rev. Roum. Chim.*, **1977**, *22*, 353.
6. N.I. Ionescu, *Bulg. Chem. Commun.*, **1992**, *25*, 39.
7. N.I. Ionescu, *Rev. Roum. Chim.*, **1992**, *37*, 509.
8. N.I. Ionescu and M. Căldăraru, *Rev. Roum. Chim.*, **2002**, *47*, 1213.
9. N.I. Ionescu and M. Căldăraru, *Rev. Roum. Chim.*, **2006**, *51*, 521.
10. R. Stechemesser, *Ber. Bunsenges Physik Chem.*, **1973**, *77*, 312.
11. A. Bielanski and J. Haber, *Catal. Rev. Sci. Eng.*, **1979**, *19*, 1.
12. M. Che and A.J. Tench, *Adv. Catalysis*, **1983**, *32*, 1.
13. N.I. Ionescu and M. Căldăraru, "Heterogeneous Selective Oxidation of Lower Olefins", Ed. Academiei Române, 1993, p. 197.
14. A. J. Tench and T. Lawson, *Chem. Phys. Lett.*, **1970**, *7*, 459.
15. N.I. Ionescu , *Surf. Sci.*, **1976**, *61*, 294.
16. N.I. Ionescu, *Rev. Roum. Chim.*, **1981**, *26*, 815.
17. N.I. Ionescu, *Z. Phys. Chemie, Neue Folge,* **1978**, *109*, 95.
18. N.I. Ionescu, *Rev. Roum. Chim.*, **1979**, *24,* 83.
19. N.I. Ionescu, *Rev. Roum. Chim.*, **1979**, *24*, 399.
20. N.I. Ionescu, *Rev. Roum. Chim.*, **1980**, *25*, 663.
21. N.I. Ionescu, *Rev. Roum. Chim.*, **1995**, *40*, 639.