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Effect of Surface Curvature of Semiconductors upon Their Adsorptive Capacity

O. PESHEV AND G. BLIZNAKOV

From the Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

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The adsorption properties of finely dispersed and finely porous semiconducting adsorbents have been investigated within the framework of the electron theory of chemisorption on semiconductors. In a pore with a radius commensurable with or smaller than the Debye radius the effects of the boundary layer are rather weakened with respect to those with a plane surface. In such a pore specific adsorptive capacity and heat of adsorption are increased. The problem of optimum porosity, related to adsorptive capacity is considered.

When discussing the influence of porosity upon the catalytic activity of solids attention has mainly been paid to diffusion. It has been assumed [Wheeler (*1*)] that "chemical behavior and catalytic action are independent of pore dimensions." This assumption introduces an essential simplification and gives the possibility of concentrating the attention on the diffusion effects only. Strictly speaking, there are no grounds for considering the chemical properties of the pores independent of their curvature, i.e., of their radius. On the contrary, this dependence is to be expected on the basis of general thermodynamic considerations. This has been shown experimentally on silica gel, aluminum oxide, and alumo-silicates. It has been established that the surface OH groups of adsorbents and catalysts of this kind are not equal in their chemical activity. Their reactivity is a function of the pore curvature (*6–10*). Dependence of the selectivity of the catalyst upon the curvature of its surface has been observed by Schwab with the decomposition of ethanol and formic acid on metal oxides and salts (*11*). Thus, there exists another side of the problem of the adsorption and catalytic activity of porous bodies—the dependence of the chemical behavior, in particular of the adsorption properties, of the pores on their radius. In this aspect the present work considers theoretically the problem of the adsorption properties of finely dispersed and finely porous semiconducting adsorbents.

I. EFFECT OF SEMICONDUCTOR DISPERSITY ON THE ADSORPTIVE CAPACITY

As shown by Kogan (*2*), the specific (per unit of surface) adsorptive capacity of a semiconducting plate depends on its dispersity S/V (S, surface; V, volume of the specimen). This effect is observed, when the ratio S/V is of the order $1/L$, where L is the Debye radius for the given specimen. In all cases specific adsorptive capacity decreases with the increasing dispersity. The physical nature of the effect is very simple. With a thick plate (linear dimensions $l \gg L$), the effect of surface charge, which spreads itself over a distance of the order of L, does not reach the depth of the crystal, the latter being in this case electrically neutral. The condition of electric neutrality determines a given position of the Fermi level. With a thin plate ($l \ll L$), the effect of surface charge "penetrates" the whole crystal. In this case, the bulk is not electrically neutral even in the middle. Surface and bulk charges are opposite in sign, which means that the

Fermi level is shifted with respect to its position in the thick plate, i.e., with acceptor surface levels downwards, and with donor levels upwards. As a result, the adsorptive capacity decreases.

With small coverage, the position of the Fermi level determines only the concentration of charged particles. For that reason the effect under consideration increases parallel with the relative amount of charged particles in the chemisorbate becoming greater.

Two of the conditions in Kogan's conclusion are of importance for the present work:

1. The number of adsorption centers per unit surface and their nature are independent of l.
2. The surface charge is made solely of chemisorbed particles.

Let us consider the case when the first condition is not fulfilled, and the free electrons or holes of the semiconductor play the part of adsorption centers. The above effect will increase, because after shifting the Fermi level in the small crystal the specific adsorptive capacity will additionally decrease, due to the diminished number of adsorption centers.

The second condition is very essential. Were it not fulfilled, this may, in some cases, cause a change of sign in the effect. Indeed, the conclusion that the specific adsorptive capacity decreases with increasing dispersity is based on the inequality deduced in (*2*)

$$d|\sigma|/dl > 0 \qquad (1)$$

which is valid at fixed outward conditions, irrespective of level positions in the bulk, and on the fact that according to the second condition $|\sigma| \sim N^-$. Here σ denotes the surface charge density, N^- is the surface concentration of charged particles, the latter being assumed to have an acceptor character. It is evident from (*2*), however, that this inequality is valid, when the spectrum of nonadsorptive levels is independent of l, regardless of whether the acceptor surface levels are of adsorption origin or not. Assuming that there is a great number of acceptor levels of nonadsorptive origin on the surface of the specimen, the relative participation of chemisorbed particles in the surface charge will be negligibly small. On the other hand, according to (1), the Fermi level in a thin specimen will be lowered with respect to its position in the semi-infinite specimen. On this basis, the sign of the effect will depend upon the kind of chemisorbed particles. It will be negative (decreased adsorptive capacity) with acceptor particles and positive (increased adsorptive capacity) with donor particles.

There exists a unique relationship between the Fermi level and the heat of adsorption Q (*3*, *4*). The equation

$$Q = q^- - \epsilon_s^- \qquad (2a)$$

is valid when the adsorbed particles have acceptor nature and the charged form of chemisorption prevails in the chemisorbate;

$$Q = q^+ - \epsilon_s^+ \qquad (2b)$$

holds, when the adsorbed particles are donors and the charged form of chemisorption predominates in the chemisorbate. Further

$$Q = q^0 \qquad (2c)$$

is valid, when the electrically neutral form of chemisorption is prevailing, regardless of whether the particles are acceptors or donors. In all these cases the specific adsorptive capacity and the heat of adsorption change as functions of dispersity, in the same sense: decrease of adsorptive capacity will be accompanied by a decrease of adsorption heat, and *vice versa*. As is evident from (2), the change of adsorption heat together with the alteration of coverage (for a given specimen) is determined by the law of changing the position of the Fermi level: $\epsilon_s^{-,+} = \epsilon_s^{-,+}(N)$, where N is the total concentration of chemisorbed particles and $\epsilon_s^{-,+}(N)$ is in most cases an increasing function.

In ref. (*2*) is considered the mono-dimensional case: a plate with a thickness l. The specific adsorptive capacity depends on the linear dimensions of the crystal, when the number of electrons localized on the surface acceptor levels becomes commensurable with the total number of electrons in the conductivity band and on the acceptor levels in the bulk (or surpasses it). With the holes, the conditions are analogous. Hence, the above results are also applied in cases when the crystals are small, two- or three-dimensional ones. This could be shown by direct calculations as well. These considerations will be used again later.

II. Effect of Semiconductor Porosity upon Adsorptive Capacity

As was pointed out, real adsorbents and semiconducting catalysts are porous bodies in most cases. In this respect, the adsorption properties of the pores in the semiconducting crystal are of interest. A cylindrical cavity with a radius R will be regarded. Let us consider the dependence of the Fermi level position on the pore surface upon the pore radius. Using the symbols given in Fig. 1 we can write

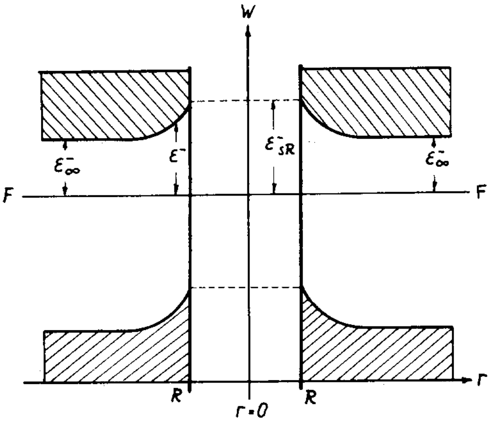

Fig. 1. Scheme of the energy bands in a semiconductor in the presence of a pore with negative charge on its surface; FF, the Fermi level.

$$Z^+ = Z_\infty \exp\frac{\epsilon^- - \epsilon_\infty^-}{kT}, \qquad Z^+ = p + n_{\mathrm{D}}^+$$

$$Z^- = Z_\infty \exp\left(-\frac{\epsilon^- - \epsilon_\infty^-}{kT}\right), \quad Z^- = n + n_{\mathrm{A}}^-$$

Here qZ^+ and qZ^- signify the densities of the positive and negative bulk charge, respectively; n_{D}^+ and n_{A}^- are the concentrations of ionized donors and acceptors in the bulk; n and p denote the concentrations of free electrons and holes. A Maxwell distribution over all local and band levels is assumed. Poisson's equation

$$\nabla^2\epsilon^- = \frac{4\pi q}{\chi}\rho \qquad \rho = q(Z^+ - Z^-),$$

(where q is the absolute value of electron charge; χ, the dielectric permitivity of the crystal; ρ, the density of bulk charge) takes with cylindrical symmetry the following form:

$$\frac{d^2\epsilon^-}{dr^2} + \frac{1}{r}\frac{d\epsilon^-}{dr} = \frac{8\pi q^2 Z_\infty}{\chi}\, sh\, \frac{\epsilon^- - \epsilon_\infty^-}{kT} \qquad (3)$$

Equation (3) can be simplified by assuming that

$$\left|\frac{\epsilon^- - \epsilon_\infty^-}{kT}\right| \ll 1. \qquad (4)$$

As will be seen further, the results are not essentially associated with this assumption. After putting

$$\frac{\epsilon^- - \epsilon_\infty^-}{kT} = \psi, \qquad \frac{r}{L} = \xi, \qquad L = \left(\frac{\chi kT}{8\pi q^2 Z_\infty}\right)^{1/2}$$

and taking into consideration Eq. (4), Eq. (3) can be written in the form

$$\frac{d^2\psi}{d\xi^2} + \frac{1}{\xi}\frac{d\psi}{d\xi} = \psi \qquad (5)$$

The additional conditions are

$$\psi = 0, \qquad d\psi/d\xi = 0, \qquad \text{when} \qquad \xi \longrightarrow \infty$$

The solution of (5), which satisfies these conditions, has the form

$$\psi = CK_0(\xi) = C(i\pi/2)H_0^1(i\xi), \qquad (6)$$

where H_0^1 is the first Hankel function of zero order, and C is a constant. Using the correlations (*5*)

$$\frac{d}{d\xi}\,\xi^\nu K_\nu(\xi) = -\,\xi^\nu K_{\nu-1}(\xi), \qquad K_{-\nu}(\xi) = K_\nu(\xi)$$

one obtains

$$d\psi/d\xi = -CK_1(\xi)$$

When $\xi \rightarrow 0$, the functions $K_0(\xi)$ and $K_1(\xi)$ display the following behavior:

$$K_0(\xi) = \ln(2/\xi), \qquad K_1(\xi) = (1/\xi), \qquad (7)$$

and with $\xi \rightarrow \infty$ (irrespective of the value of ν), it will be valid

$$K_\nu(\xi) = (\pi/2\xi)^{1/2}\exp(-\xi) \qquad (8)$$

On the basis of the electric neutrality of the system pore–crystal and after applying the Gauss theorem one obtains

$$\left(\frac{d\psi}{d\xi}\right)_{\xi=R/L} = \frac{4\pi q\sigma L}{\chi kT}$$

hence

$$C = -\frac{4\pi q\sigma L}{\chi kT K_1(R/L)} \tag{9}$$

Let us consider the following two limiting cases:

(a) A wide pore $(R/L) \gg 1$

On the basis of (9), (8), and (6) one obtains

$$\psi = \psi_{s\infty}\left(\frac{R/L}{\xi}\right)^{1/2} \exp\left[-\left(\xi - \frac{R}{L}\right)\right]$$

The magnitude

$$\psi_{s\infty} = -\frac{4\pi q\sigma L}{\chi kT} \tag{10}$$

denotes the bending of energy bands on the plane surface of a semi-infinite crystal, caused by a surface charge of the same density σ. It is evident that

$$\psi(R/L) \equiv \psi_{sR} = \psi_{s\infty}$$

i.e., the surface of a wide pore behaves practically as a plane surface.

(b) A narrow pore $R/L \ll 1$.

Taking (9) and (7) into account, one can write

$$\psi = -\frac{4\pi q\sigma L}{\chi kT}\frac{R}{L}K_0(\xi) = \psi_{s\infty}\frac{R}{L}K_0(\xi) \tag{11}$$

Considering (7), we obtain

$$\psi(R/L) \equiv \psi_{sR} = -\psi_{s\infty}(R/L)\ln \tfrac{1}{2}(R/L) \tag{12}$$

The factor $-(R/L)\ln\frac{1}{2}(R/L)$ increases monotonously from 0 to $2/e \approx 0.74$ within the range of $0 \leq R/L \leq 2/e$. The bending, ψ_{sR}, of the energy bands on the surface is, therefore, with a narrow pore $(R/L \ll 1)$ much smaller than with a plane surface. In other words, the boundary layer effects in a narrow pore are rather weakened. This means that one and the same concentration of negatively (positively) charged particles will lower (raise) the Fermi level on a plane surface much more so than in a narrow pore. It follows immediately that the specific adsorptive capacity in a narrow pore is increased with respect to that on a plane surface under the same outward conditions, while, according to (2), the heat of adsorption is increased.

This effect is opposite to the one described by Kogan. Its physical nature is simple and expressed by the formulas (12), (11), (7): The narrow pore behaves in fact as a charged filament, which is evident from the logarithmic course of potential at small $(\xi \ll 1)$ distances. Since the density of the surface charge σ is assumed to be constant and independent of R, the linear density of charge of this filament will be proportional to the radius of the pore [the factor R in Eqs. (11) and (12)]. Hence, the narrower the pore the more negligible will be the bending of the bands. Assumption (4) means in fact that the value of density of surface charge is not great [see Eq. (10)]. It is evident, however, that this assumption is not of great importance for the above results.

III. Conclusion

The obtained results show that specific (and total) adsorptive capacity of a semiconducting adsorbent is greater, when the latter has a finer porous structure. It must be taken into account that when the number of narrow pores becomes so great that the average wall thickness is commensurable with the pore radius, conditions are created favoring the effect of decreasing the specific adsorptive capacity. Under these conditions the effect of surface curvature is compensated by the effect of the thin walls (Kogan's effect). With pores having very thin walls this latter effect predominates. Hence, with respect to adsorptive capacity, an optimum porosity of semiconducting adsorbents may exist.

The above results must be taken into consideration in studying the relationship between chemisorption and electrophysical properties of semiconductors. For example, work function measurements by the contact potential method do not account for changes of position of the Fermi level in the pores. But it is these changes which determine the course of chemisorption.

In conclusion, it is clear that when chemisorption (or chemidesorption) is a rate-determining stage and the influence of diffusion can be neglected, the above-described effects may be of importance for the catalytic activity as well.

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