Translated from *Uspekhi Khimii* **58** 881–907 (1989) U.D.C. 541.128.3

The influence of electric fields on the chemisorption and catalytic properties of semiconductor catalysts

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ABSTRACT. Studies of the influence of electric fields on the chemisorption and catalytic properties of semiconductor catalysts, carried out in order to test the principal postulates of the electronic theory of catalysis, are examined. It is shown that, because of the high density of the surface states, the possibility of the electronic control of the surfaces of polycrystalline catalysts by the field effect method is extremely limited. Possible ways of regulating the chemisorption and catalytic activities of solid catalysts with the aid of an external electric field are discussed: (1) the change in the concentration of polar molecules in strong inhomogeneous local fields near the surface; (2) the activation of surface compounds by "hot" electrons; (3) the modification of the defective structure when the concentration of cations in the surface layers of oxide catalysts is altered; (4) surface doping of film catalysts by alkali metals from the dielectric support during their electrolytic deposition.

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Introduction

In chemical thermodynamics the external electric field is considered, like pressure and temperature, as an additional thermodynamic parameter influencing the rate and equilibrium constants for a chemical reaction. The principal aspect of the utilisation of electric fields in catalysis is at the junction between catalysis and electrochemistry and has been the subject of a special branch of chemistry—electrocatalysis. The need to solve practical problems—the creation of highly effective hydrogen and oxygen electrodes, the search for low-temperature hydrocarbon oxidation catalysts, the intensification of various reactions involved in the electrosynthesis of organic and inorganic compounds, and also the additional possibilities for the investigation of the mechanism of catalysis by electrochemical methods—have stimulated a large number of studies in the field of electrocatalysis, the principal results of which have been surveyed in a series of reviews[1–4] and monographs.[5,6]

Very strong fields are used in the study of surfaces by the autoelectronic and autoionic microscopic methods. These methods make it possible to obtain an image of the surface and the use of an atomic probe or a mass spectrometer also permits the study of the chemical composition of the surface and of a wide variety of reactions occurring in extremely strong electric fields at the tip of the emitter. The field-stimulated surface reactions have been analysed in a series of reviews.[7–10]

Finally, as the electronic ideas have developed, yet another aspect of catalysis has arisen—the employment of the field effect method in the study of the chemisorption and catalytic properties of semiconductors.

The idea that free carriers are involved in chemisorption and catalytic properties appeared in connection with the experimental observation of the dependence of the electrophysical parameters of semiconductors (electrical conductivity, electron work function, and the Hall constant) on the gaseous and environment. The theoretical foundations of the electronic theory of catalysis were laid in the studies of Vol'kenshtein [Wolkenstein],[11] Hauffe,[12] German,[13] and other workers. The use of quantum-statistical methods for the description of surface phenomena made it possible to discover the role of the Fermi level as a "collective" factor influencing the chemisorption and catalytic properties of semiconductors. Hence follows directly the possibility of regulating the activity of catalysts via external influences such as the introduction of heterovalent additives[14–16] and the application of an external electric field, which shifts the position of the Fermi level on the semiconductor surface.

The change in the chemisorption and catalytic properties of semiconductors following the application of an external electric field was predicted theoretically by Vol'kenshtein as early as 1955.[17] The electroadsorption effect was first observed experimentally in a study[18] where an increase in the hydrogen and carbon monoxide pressure was noted when a positive potential was applied to a germanium film specimen. At the present time the influence of the field on chemisorption and catalytic properties has been observed also in other studies. In view of the fundamental importance of these results for the confirmation of the electronic theory of catalysis, they have been described in many monographs and review articles devoted to the physical chemistry of the surfaces of semiconductors.[11,19–21]

In semiconductor physics, the field effect method has been given a theoretical justification. It has found technical applications in connection with the use of sufficiently perfect single crystals with the lowest concentration of surface states at the semiconductor–dielectric interface. However, the majority of the adsorption and catalytic studies in which the field effect method was applied have been carried out on polycrystalline specimens with a high concentration of surface states, which exceeds by several orders of magnitude the

density of the field-induced charge. Under such conditions, it is impossible to expect any appreciable shift of the position of the Fermi level or a change in the charge state of the catalytic reactive centres. In most studies, qualitative results concerning the effect of the field on adsorption and catalysis were presented without a comparison of the orders of magnitude of the observed effect with the concentration of the field-induced charge and the possible shift of the surface potential. It is striking that, despite the entire wide variety of the condenser designs and conditions (temperature, pressure, electric field strength, material of the dielectric) used, different secondary influences by the field on the heterogeneous catalytic system were as a rule not taken into account.

The aim of the present review is a critical examinaion of the results of studies of the chemisorption and catalytic properties of semiconductors by the field effect method with allowance for the physicochemical phenomena arising in systems when an external field is applied and the discussion of the possible mechanisms of the observed effects and the ways in which the electric field influences the adsorption and catalytic processes.

Henceforth the terms "electroadsorption" and "electrocatalysis" will be understood to imply the influence of an external field on the chemisorption and catalytic processes regardless of the mechanism involved in the action of that field. The electric field strength used in the field effect method is determined by the breakdown strength of the dielectric and does not exceed 3×10^8 V m^{-1}, but, owing to the roughness of the relief, near the surface the field strength may greatly exceed the average value calculated from the geometry of the condenser. We shall therefore consider briefly below the mechanisms of the influence of a very strong field on a heterogeneous gas–solid catalytic system.

II. The possible mechanisms of the influence of a very strong electric field ($>10^8$ V m^{-1}) on a heterogeneous gas–solid catalytic system

The electroadsorption and electrocatalytic effect in a gas-solid system may be determined both by the change in the state of the gas and solid molecules in the external field and by the influence of the field on their interaction. The effect of the field on a heterogeneous catalytic system is based on the following physical phenomena.

1. The change in the potential energy of the electrons of the atoms, molecules, and ions formed in the autoionisation process in a very strong external field (5×10^9–5×10^{10} V m^{-1}).
2. The formation of a system of dipoles oriented by the field.
3. The change in the electron work function of the solid as a consequence of the influence of the field on the electrostatic image forces.
4. The appearance of a mechanical stress, directed at right angles to the surface of the solid, when the electric field is applied.

We shall consider the mechanisms of the influence of the field on adsorption and catalysis determined by these phenomena.

The possibility of altering the properties of a heterogeneous catalytic system under the influence of very strong fields ($>5 \times 10^9$ V m^{-1}), comparable to intraatomic fields, is not open to doubt. Quantum-mechanical calculation performed for a series of gas molecules have shown[22,23] that, for $E > 5 \times 10^9$ V m^{-1}, the electron density is redistributed and this is accompanied by a change in the effective charges on atoms, in the bond lengths and angles, and in the ionisation potentials and electron affinities and hence by a change in the reactivity of the molecules. A simple diatomic adsorbate–support model in an external electric field has been calculated[24] by the LCAO method. An effect of the field on the bond energy, the equilibrium position, and the vibration frequencies of the adsorbate has been observed for $E > 10^9$ V m^{-1}. The energies of the bonds formed on chemisorption of the H_2O and CO molecules on NaCl and MgO(001) have been given[25] as a function of the adsorbate–support distance in the presence of an external field. It has been shown that the field alters not only the electrostatic but also the exchange energy of the interaction of the adsorbed molecules with the surface of ionic crystals.

In the strong electric field ($\sim 10^{10}$ V m^{-1}) arising at the tip of the ion emitter, atoms and molecules are ionised due to the quantum-mechanical tunnel electron transfer through the barrier generated by the field and the image forces in the metal.[8–10,26] The change in the form of the potential curve for the ion near the surface of the solid when an external $\sim 10^{10}$ V m^{-1} field is applied can lead (depending on the sign of the field) either to the stabilisation of the surface ionic structures or to the desorption of the ion by the field. Analysis of the chemical composition of the surface by the method involving the desorption of ions by the field using a time of flight atomic probe or an ionic field mass spectrometer have made it possible to observe various reactions occurring in the presence of strong electric fields. The following types of reactions have been quoted in a review.[9]

(a) Proton or cation exchange in the ionisation of gas molecules near the surface.

(b) The formation of complex ions on interaction of various gases with metallic emitters.

(c) The decomposition of molecules into fragments under the influence of the field.

(d) The ion–molecule reactions which can be initiated by radicals, radical-ions, or molecules in ionised states.

The study of the elementary processes occurring under the influence of very strong fields is of definite interest also for catalysis in the absence of an external field, because fields with $E \simeq 10^9$ V m^{-1}, generated by the ionic lattice of the solid, are then present over the surface of catalysts.[27]

For $E < 5 \times 10^9$ V m^{-1}, where the changes in the quantum-mechanical parameters of the molecules under the influence of the field become insignificant, the influence of the field on the adsorption and catalytic processes can be determined by polarisation effects. On polarisation in an external electric field, molecules with a dipole moment μ and a polarisability α receive an additional energy $\mathscr{E} = \mu E + {}^1/_2 \alpha E^2$, which results in their preferential orientation in space in the direction of the field, which cannot fail to affect the energy of the bond between the adsorbed species and the catalyst surface.

The dependence of the coverage of the tungsten tip of an [field ion] emission microscope by oxygen and alkali metal atoms on the field strength near the tip has been investigated.[28–30] The state of the surface before and after adsorption and also the change in the degree of adsorption under the influence of fields of different polarity were characterised by the electron work function of the tip determined from the Fowler–Nordheim relation between the emission current and the applied potential. It was observed that the degree of surface coverage by metal atoms under the influence of a field having a positive polarity increases and that under the influence of a field with a negative polarity diminishes. In relation to oxygen, the electron adsorption effect has the opposite sign—additional adsorption of oxygen on the tungsten tip is observed when a field with a negative polarity is applied. The results

obtained make it possible to represent the metal and oxygen atoms adsorbed in a charged form as dipoles with effective dipole moments μ^* and polarisabilities α^*, the heat of adsorption of which changes in the presence of the field E by an amount $\Delta q = \mu^* E + {}^1/_2 \alpha^* E^2$. With increase in the degree of coverage and hence with decrease in the proportion of the charged form of the chemisorbed species, the influence of the field on the chemisorption weakens and the effective values of μ^* and α^* diminish in the general case.

The changes in the state of the gas phase after the application of an external field can also be described by means of a thermodynamic approach[31] taking into account the influence of polarisation and spatial orientation processes on the entropy and the internal and free energies of the reactants and products of the chemical reaction and hence on its rate and equilibrium constants. The change in free energy per unit volume of the dielectric after the application of a field E is $\Delta \mathscr{F} = {}^1/_2 \varepsilon_0 \varepsilon_D E^2$. If the dielectric constants ε_D of the reactants and products are not the same, there is a possibility of a shift of the thermodynamic equilibrium in the system. According to the data of Block and Moentack,[32] the change in the equilibrium constant K as a function of the electric field strength E is determined by the relation

$$\partial \ln K / \partial E = \Delta M / kT,$$

where ΔM is the difference between the field energies of all the species in the field E before and after the reaction:

$$\Delta M = \left[\sum \mu_p - \sum \mu_r\right] E + {}^1/_2 \left[\sum \alpha_p - \sum \alpha_r\right] E^2.$$

(The subscripts r and p refer to the reactants and products of the reaction respectively).

The change in the reaction rate constant as a result of the decrease in the entropy of the dipolar molecules in the gas phase or in the adsorption layer, caused by the freezing of the rotational degrees of freedom in the electric field, has been estimated.[33] For a limited rotational freedom of the activated complex, this increases the reaction rate constant in the field $E = 9 \times 10^9$ V m^{-1} by a factor of 10^2–10^4. Evidently the polarisation effect can have an appreciable influence on the thermodynamic state of the gas phase and on the rate of chemical processes in a field $E > 10^9$ V m^{-1}, where the field energies of the species exceed kT. For example, $\mathscr{E} \simeq kT$ for a water molecule with $\mu = 1.8$ D and $\alpha = 1.46$ Å when $E = 3 \times 10^9$ V m^{-1}. When $E < 10^8$ V m^{-1}, the polarisation effects may be neglected.

Another thermodynamic parameter which changes in the presence of an inhomogeneous electric field is the pressure exerted by a gaseous dielectric on the surface of the solid catalyst. In the space near the electrode, the polarised gas molecules are acted upon by the force

$$\mathscr{F} = (\mu + \alpha E)\, dE/dr,$$

which is proportional to the electric field strength gradient dE/dr and which varies as the density of the flux of species incident per unit area per unit time and of the momentum given up by the molecules to the solid.[7] The multilayer adsorption of water vapour ($\sim$100 monomolecular layers) on a tungsten tip has been observed[34] at high electric field strengths ($E > 10^9$ V m^{-1}) and a low vapour pressure ($p_{H_2O} = 10^{-3}$ Pa) in the chamber of an ion emitter. The condensation of water vapour under such conditions can be explained by the increase in the pressure p_{H_2O} by several orders of magnitude near the tip as a result of the force acting on the dipolar H_2O molecules in the field direction. The sharp increase in surface coverage of a germanium cathode by oxygen in a field with the autoionic sign whose strength exceeds 1.39×10^{10} V m^{-1} has been noted.[35] The authors attribute this threshold effect to the possibility that the oxygen molecule may overcome the activation barrier in adsorption on a germanium tip as a result of the energy aquired in the inhomogeneous electric field. The increase in the surface coverage of the catalyst by the reactants under the influence of the electric field can alter the kinetics and mechanism of the catalytic process.

The external electric field can act both on the local properties of the solid catalyst and on the electron work function as a consequence of the Schottky effect. The decrease in the electric image forces in the presence of the external field reduces the overall electron work function by an amount $\Delta\chi = e^{3/2} E^{1/2}$ and is observed from the increase in the thermal electron and autoelectron emission currents and also from the increase in the degree of surface ionisation.[36] The surface ionisation and ion adsorption and desorption processes induced by the field can influence the rate of homogeneous-heterogeneous catalytic reactions. As an example, one may quote the decomposition of ammonia on the Pt–Rh–Pd catalyst in an electric field.[37] When a negative potential was applied to the catalyst, an increase in the rate of decomposition of NH_3 by a factor of 1.5–2 was observed with a simultaneous decrease in temperature and the conductivity of the specimen. The mechanism of the action of the field was attributed by the authors to the field-induced desorption of the negatively charged species, which accelerates the gas-phase processes. The field thereby prevents the species recombination processes on the surface, as a result of which the temperature on the catalyst surface decreases.

The changes $\Delta\chi$ become appreciable for fields with $E > 10^8$ V m^{-1} and should have a significant influence on the rates of reactions in which the electronic transitions between the solid and the surface species constitute the rate-limiting stage of the reaction. The study of the dependence of the activation energy for the decomposition of formic acid and of the rate of the latter on the electron work function of the catalyst, altered by an external electric field, has been undertaken.[38] A silver wire 2.5×10^{-5} m in diameter, serving as the internal electrode of a cylindrical condenser, was used as the catalyst. The changes in the electron work function $\Delta\chi$ after the application of the field were detected reliably by measuring the autoelectron emission currents. In conformity with earlier results,[39] it was assumed that the catalytic decomposition of formic acid should be accelerated by a field with a positive polarity of the silver catalyst and should be inhibited by one with a negative polarity. However, experiments showed that an irreversible decrease in the rate of reaction takes place in both cases. The authors explained this result by an increase in the roughness of the catalyst surface and a change in its structure when the reaction takes place in the presence of the field.

The mechanism of the change in the structure of the catalyst surface in an external field is apparently complex, but, when $E > 10^9$ V m^{-1}, the mechanical stress $\sigma_E = {}^1/_8 \pi \varepsilon_0 E^2$, arising under the influence of mechanical forces and directed at right angles to the electrode surface, plays an important role. In fields with $E = (3$–$5) \times 10^9$ V m^{-1}, whereupon the energy imparted by the field to the gas molecules is comparable to kT, the mechanical stress $\sigma_E = 10^6$–10^7 Pa can induce the plastic deformation of the surface layers of the solid.[40]

Thus, despite the wide variety of the mechanisms of the action of fields with $E > 10^9$ V m^{-1} on the catalytic system (the rearrangement of the molecular and surface structures, the change in the energy of the bond between the adsorbate and the surface, the dependence of the rate and equilibrium constants for a chemical reaction on the field, the increase in the gas pressure near the catalyst-electrode, and the influence of the field on the electronic transitions between the solid and the adsorbed species, and the desorption of ions by the field), the possibility of using very strong fields in catalytic studies is limited as a consequence of the degradation of the catalyst surface by the field.

III. The influence of the electric field on the chemisorption and catalytic processes occurring on semiconductor catalysts

1. The mechanism of the influence of the electric field on chemisorption and catalysis from the standpoint of the electronic theory

In the case of a semiconductor catalyst, the influence of the field on chemisorption and catalytic processes can be associated with the shift of the position of the Fermi level on the semiconductor surface when an additional surface charge is induced by the field. This possibility has been examined in the electronic theory of catalysis.[11,41,42] According to the electronic theory,[11] the gas molecules are adsorbed on the surface of the semiconductor catalyst in neutral and charged forms, between which transitions are possible. The probability that a species exists in the charged or neutral state and also the degree of surface coverage of the adsorbent under the conditions of thermodynamic equilibrium, when adsorption equilibrium between the gas phase and the surface and the electronic equilibrium between the bands and the surface state have been attained, is determined by the position of the Fermi level at the surface of the semiconductor catalyst.[11] The species chemisorbed in the donor, acceptor, and neutral forms differ in their reactivities. The Fermi level, by determining the concentration of the active form, is thus a regulator of the rate of the catalytic reaction. The rate of reaction may depend on the position of the Fermi level also in the case where the intermediate surface compounds are formed with participation of the conductivity electrons of the solid.[43] Hence follows the possibility of a change in the adsorption capacity and catalytic activity of the semiconductor catalyst after the application of an external field, which alters the concentration of the free carriers in the surface region of the semiconductor and hence the level of the chemical potential of the electrons.

The relative changes in the chemisorption capacity and catalytic activity induced by the electric field are defined by the following relations according to the data of Baru and Vol'kenshtein:[42]

$$\Delta N/N_0 = (N - N_0)/N_0 = \eta_0^{\mp} \{\exp[\mp (V_s - V_{s0})] - 1\}, \quad (1)$$

$$\Delta g/g_0 = (g - g_0)/g = \exp[\mp (V_s - V_{s0})] - 1, \quad (2)$$

where N and N_0 are the total numbers of species of the given kind chemisorbed on a unit surface under the conditions of equilibrium in the gas phase when the field is applied and in its absence, $\eta_0^{\mp} = N_0^{\mp}/N_0$ is the relative content of the charged form on the surface for $E = 0$, g and g_0 are the rates of reaction when the field is applied and in its absence, and $V_s - V_{s0}$ is the change in the surface potential (in units of kT) equal to the shift of the position of the Fermi level on the surface of the specimen following the application of the field; $(V_s - V_{s0}) > 0$ corresponds to an increase in the electron work function after the induction of a positive charge in the semiconductor and $(V_s - V_{s0}) < 0$ corresponds to its decrease after the introduction of a negative charge into the semiconductor.

It follows from Eqns. (1) and (2) that the field inducing a negative charge in the semiconductor and shifting the level of the chemical potential on the specimen surface upwards relative to the edge of the band increases the degree of adsorption of acceptors (and also accelerates the acceptor reaction) and diminishes the degree of adsorption of donors (inhibits the donor reaction). The field inducing a positive charge in the semiconductor acts in the opposite way. The form of the functional dependence of $\Delta N/N_0$ and $\Delta g/g_0$ on $V_s - V_{s0}$ shows that the positive effect increases with increase in the displacement of the surface potential, while the negative effect is expressed by the asymptotic approach of $\Delta N/N_0$ to $\eta_0^{\mp}$ and of $\Delta g/g_0$ to -1. Consequently the electrodesorption effect is limited by the relative contribution of the charged form of chemisorption before the application of the field.

2. The change in the bending of the bands of on the surfaces of semiconductors under the influence of an external electric field

The conclusion arising from the electronic theory that the chemisorption and catalytic activities of semiconductors can be regulated by an electric field has been tested experimentally. The change in the concentration of free carriers in the surface region of the semiconductor catalyst was achieved by applying a potential difference to a condenser one of the plates of which consisted of the semiconductor investigated. The wide variety of condenser designs employed is striking (Fig. 1) A plane-parallel condenser has been used in a number of studies[44–49] (Figs. 1*a*, 1*c*, and 1*e*), while the role of the dielectric plate was assumed by a vacuum (gas) or a mica plate. The principal deficiency of condensers having this design is the presence of a field in the gas phase at the surface of the adsorbate, which requires special precautions to avoid their discharge and the ionisation of the gas.

A condenser design free from this disadvantage has been proposed[18] (Figs. 1*b* and 1*f*). A thin film specimen, whose thickness d is smaller than the Debye shielding length L, is sputtered onto a support which serves simultaneously as the dielectric plate of the condenser; a metallic electrode is deposited on the other side of the support. Condensers having this design have been used in a number of studies[18,50–71] and it has been shown[72] that, when the condition $d < L$ holds, the application of the field should alter the position of the Fermi level and the degree of filling of the surface states by electrons not only from the inner side of the film but also from its outer side directed towards the gas phase.

Cylindrical condensers with a gap above the catalyst surface have been used to investigate the influence of the field on chemisorption and catalytic processes at elevated temperatures and pressures (from 2×10^3 to 10^5 Pa)[73–77] (Figs. 1*g* and 1*h*). In order to avoid discharge processes in the gas phase and the electrical breakdown of the dielectric, the field strength between the condenser plates was kept at a value not exceeding 10^6 V m^{-1} and the charge induced in the semiconductor was $e\Delta n_v \leqslant 5 \times 10^{13}$ el. charge m^{-2}. In a number of studies,[44–46,50–54] electroadsorption has been investigated at room temperature and low adsorbate pressures (0.5 Pa), which made it possible to increase the field strength to 2×10^7–2×10^8 V m^{-1} and the induced charge to 10^{15}–10^{16} el. charge m^{-2}.

A quantitative comparison of the experimental results for the influence of the field on chemisorption and catalytic processes with theoretical data derived from Eqns. (1) and (2) of the electronic theory is possible, provided that the dependence of the shift of the surface potential (V_s–V_{s0}) on the electric field strength E is known. The dependence of V_s on E cannot be obtained purely theoretically from the solution of the Poisson equation because a large part of the charge induced by the field is captured by the surface state of the semiconductor and the shift of the surface potential is much smaller than the theoretically possible value. The field effect method has been developed in detail for germanium and silicon single crystals.[78–80] This method makes it possible to calculate from the experimental field effect curve the bending of the bands on the surface and the charge captured by the surface state as a function of the field-induced charge.

Most of the studies of the influence of the field on chemisorption and catalytic processes have been carried out on polycrystalline semiconductor specimens, an exact calculation of the electrophysical parameters of the surface of which as a function of the electric field strength is impossible. The relation obtained by Many et al.[80] has been used by Deren and Mania[75] to estimate the order of magnitude of the bending of the bands after the application of the field:

$$V_s - V_{s0} = eLE \tag{4}$$

where L is the Debye shielding length:

$$L = (\varepsilon_0 \varepsilon_n kT/2\pi e^2 n_0)^{1/2}, \tag{5}$$

where ε_n and ε are the dielectric constants of the semiconductor and the dielectric, n_0 is the concentration of free carriers in the semiconductor, and e is the charge of the electron. The field strength in the semiconductor E_n is linked to the field strength in the dielectric E by the electrostatic relation

$$E_n = (\varepsilon/\varepsilon_n) E. \tag{6}$$

One should bear in mind that such a shift of the surface potential is established in the first instant after the field has been switched on and then, as the charge is captured by surface states, the quantity V_s–V_{s0} can decrease appreciably. Virtually all the semiconductors investigated are characterised by a high density of surface states.

On a germanium single crystal, the density of fast and slow states is 10^{16} m^{-2}, but increases after the adsorption of water, *p*-benzoquinone, and diphenylamine vapours to 10^{18} m^{-2} and above.[81,82] On epitaxial PbS films, the concentration of slow states *in vacuo* is 10^{17} m^{-2}.[83] Evidently the density of surface states on polycrystalline specimens should be even higher. The shift of the Fermi level on the outer side of the film after the application of an electric field to its reverse side has been determined by the conductimetric and the contact potential difference methods in a study[57] carried out on polycrystalline TiO_2 films deposited on mica supports (the condenser illustrated in Fig. 1*b*). It was shown that a thin film of reduced TiO_2 (~500 A) provides an almost complete shield against the field and the change in the contact potential difference is much lower than the theoretical value, which indicates a transfer of a considerable proportion of the induced charge to the surface states.

A large proportion of studies of the influence of the field on the chemisorption and catalytic properties of semiconductors have been carried out on polycrystalline zinc oxide specimens.[48,50,51,66–68,76] The field effect on ZnO single crystals and polycrystalline film specimens *in vacuo* has been observed by a number of workers.[84–91] Estimating the mobility of the field effect with different initial conductivities of the specimen, Heiland[85] calculated the density of surface states per unit energy range in the vicinity of the Fermi level: $S_{EF} = 10^{18}$ m^{-2} eV^{-1}. Later S_{EF} was regarded[92,93] as the "effective" density of capture centres taking into account the fact that a proportion of the states undergoing charge transfer after the application of an electric field or on illumination exist not on the surface but in the region of the space charge. The nature of the capture centres for the free carriers is apparently immaterial for the estimation of the shift of the Fermi level following the application of the external field. Bearing in mind that the field-induced charge $e\Delta n_V$ is equal to the sum of the charges $e\Delta n_{ss} + e\Delta n_c$ ($e\Delta n_{ss}$ and $e\Delta n_c$ are respectively the density of the charge transferred to the capture centres and the charge participating in the conduction by the

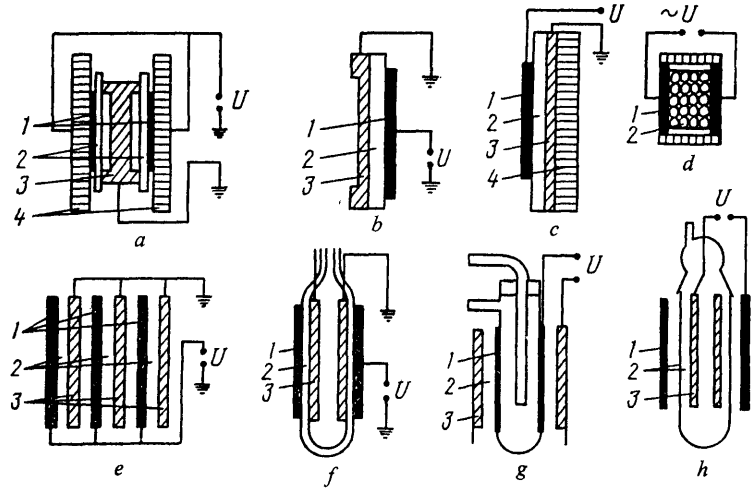


Figure 1. Design of the condensers used in the study of the influence of an external electric field on the chemisorption and catalytic properties of semiconductors: *1*, field electrodes; *2*, layers of dielectric; *3*, test specimens; *4*, support or holder.

specimen) and that we have $e\Delta n_c \ll e\Delta n_{ss}$ so that $e\Delta n_V \simeq e\Delta n_{ss}$, it is possible to estimate the shift of the Fermi level provided that the density of states S_{EF}, per unit energy range, is known:

$$V_s - V_{s0} = \Delta n_V / S_{EF}. \quad (7)$$

Henceforth, in order to discriminate between the mechanisms of the effect of the field on the chemisorption and catalytic properties of polycrystalline semiconductors, the observed effects will be compared with the changes in the surface potential $V_s - V_{s0}$ (possible for the field strengths E and the concentrations of the field induced charge $e\Delta n_v$ employed) calculated with the aid of Eqns. (4) and (7).

3. The electroadsorption of gases on semiconductor adsorbents

(a) The electroadsorption of oxygen and methanol and water vapours on a germanium single crystal

The classical field effect method[78–80] has been used to investigate the influence of the field on the adsorption of oxygen and methanol and water vapours on a germanium single crystal.[44–46] It is noteworthy that the surface properties of germanium, studied by many investigators,[21,78–80] are by no means described by the simple ideal crystal model with a local level of the adsorbed molecule, which has served as the basis of Vol'kenshtein's electronic theory. On a "real", i.e. oxidised, surface of the germanium single crystal[78] one observes a high concentration of fast and slow states of adsorption or biographical origin. By virtue of the cooperative character of the local fields, the curves for the charge capture by both fast and slow surface states, which depend on the surface potential, are monotonic.

In the adsorption of different molecules, the local surface levels are not manifested, but the energy spectrum shifts smoothly towards an increase in the concentration of slow surface states. Kiselev[94–97] proposed a donor–acceptor mechanism of the charging of the surface in adsorption, which is based on the idea that the adsorbed molecules interact with "defective" surface atoms. When an adsorption complex is formed, the electrophysical parameters of the defect change, as a result of which it is converted into a hole or electron capture centre and the localisation of the charge influences in its turn the character and strength of the bond. The chemisorption of the charged form alters the bending of the bands on the semiconductor surface, which entails a redistribution of the charge between the levels of the chemisorbed species and the levels of the biographical defects. The redistribution of the charge between the fast and slow surface states of biographical and adsorption origin and the continuous character of the energy spectrum complicate the observation and interpretation of the electroadsorption effect.

Since the surface of the germanium single crystal (2×10^{-4} m^2) is small, manometric adsorption measurements were not performed and the electroadsorption effect was estimated from the sign and magnitude of the change in the surface charge after the adsorption of the gas in the presence of the field.[44–46] The condenser illustrated in Fig. 1*a* was used in these studies. It is striking that the electroadsorption depended on the method used for the preliminary treatment of the surface of the germanium single crystal. By varying the etching conditions, two types of surface were obtained. For the same geometry of the condenser, gas pressure, and electric field strength, the electroadsorption of oxygen was observed on a type II surface but was absent on a type I surface. On the other hand, methanol vapour was adsorbed in the presence of the field only on the type I surface. This must be regarded as proof that the electroadsorption of gases is not associated with the discharge in the gas phase but is determined by phenomena occurring on the surface of germanium in the presence of the field.

The influence of a field with negative polarisation, which increases the number of electrons on the surface, on the adsorption of O_2 was observed on incompletely oxidised type II germanium specimens with a high density of slow acceptor states (there were no slow donor states on these specimens). After the field had been switched off in an oxygen atmosphere, the steady relaxation of the reverse electron transition to the bulk of germanium from the slow acceptor states, which are apparently centres for the adsorption of O_2, increased (compared with a vacuum). This induced an increase in the negative surface charge (Fig. 2). An increase in the positive surface charge has been detected on type I specimens, having the structure of the "real" surface and a high density of slow donor states, in the adsorption of methanol vapour under conditions involving the application of a field with positive polarity to the specimen.

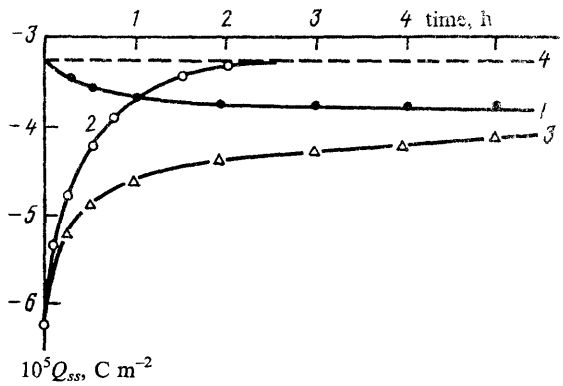


Figure 2. Relaxation of the surface charge: *1*, in the adsorption of O_2; *2*, when the field is switched off *in vacuo*; *3*, when the field is switched off in an oxygen atmosphere; *4*, the charge on the surface conditioned *in vacuo*.

A quantitative comparison of the change in the positive charge of the surface with the shift of the Fermi level has been carried out[46] in relation to the electroadsorption of water vapour using a pulse method, which is free of the disadvantages of the field effect method at a constant potential such as the inconstancy of the shift of the Fermi level as a function of time, the filling of surface states of non-adsorption origin, and appreciable changes in the surface potential of the opposite sign when the field is switched off. The amplitude, duration, and Q-factor of the pulses were chosen so that the switching on of the pulse field *in vacuo* did not change the surface charge of the specimen heated at 450 K. When a pulsed field with a positive polarity is applied to germanium in the presence of water vapour, the positive surface charge accumulates, the accumulation effect increasing with increase in the amplitude of the pulses. In a pulsed field with the opposite polarity, a decrease in the positive surface charge was observed with a tendency towards saturation as the amplitude of the pulses rose.

The experimental dependence of the change in the positive surface charge ΔQ_V in the adsorption of water vapour on germanium in a field with a positive polarity applied to the specimen (measured after the completion of the rapid relaxation process) on the change in the bending of the bands (V_s–V_{s0}) is described by the relation[46]

$$\Delta Q_V = \text{const} \cdot \exp(V_s - V_{s0}). \quad (8)$$

The results of the study of the electroadsorption of water and methanol vapours on germanium have been examined by Kiselev[94–96] from the standpoint of the donor–acceptor model. According to these data,[94,95] the CH_3OH and H_2O vapours are adsorbed on an oxidised germanium surface via a coordination mechanism in the vicinity of surface defects, which serve as capture centres for holes from the bulk of the semiconductor. The localisation of a hole near a coordinated water molecule should result in the unshared electron pair being pulled even further to the adsorption centre and in an increase in bond strength. A field increasing the concentration of holes on the semiconductor surface should promote the adsorption of water molecules, while a field with the opposite polarity should induce their desorption.[94–97] In later studies,[98,99] the accumulation of the positive surface charge was explained by the protonation of H_2O. According to Kiselev and co-workers,[98,99] the localisation of a hole in a slow state increases the effective dipole of the adsorbed complex, increases the amount of ionic character of the bond, and decreases the activation energy for the heterolytic dissociation of H_2O. These processes can be regulated by altering the electronic state of the surface with the aid of an external electric field. The number of protonated water molecules increases exponentially with increase in the shift of the surface potential (V_s–V_{s0}) in the presence of the field.

(b) The electroadsorption of O_2 on polycrystalline ZnO films

The influence of field on the adsorption of oxygen has been investigated on β-HgS films[47] and polycrystalline ZnO specimens.[48,50,51,56] A condenser with a mica plate, illustrated in Fig. 1*c*, where the maximum field strength was 10^7 V m^{-1}, has been used.[47] In order to observe the effect, measurements were made of the resistances of the specimens in the adsorption of O_2 with the field applied to the specimen. The adsorption of oxygen ($p_{O_2} = 5 \times 10^{-1}$ Pa) was accompanied by an increase in the resistance of the β-HgS film exhibiting *n*-type conductivity. When a field increasing the concentration of electrons in the semiconductor was subsequently switched on, the resistance of the specimen σ fell and, after it had been switched off, the resistance acquired a value appreciably exceeding σ before the application of the field. This result has been explained[47] by the transition from the neutral form of chemisorption to the charged form as a consequence of the additional capture of electrons by centres with chemisorbed oxygen.

The additional increase in the resistance of the specimens after the adsorption of oxygen with the field applied to the specimen has been observed by Hoenig and Lane[48] and Constantinescu et al.[56] Hoenig and Lane[48] used a condenser with an air gap (Fig. 1*c*), low field strengths $E_{max} = 5.6 \times 10^5$ V m^{-1}, and an induced charge concentration $E\Delta n_V = 2 \times 10^{13}$ el. charge m^{-2}. Under these conditions, the shift of the Fermi level, estimated according to Eqn.(7), is $\sim 2 \times 10^{-5}$ eV and the influence of the collective factor on the adsorption of gases may be disregarded because it is insignificant.

The fact that the additional increase in the resistance of the ZnO film in the presence of oxygen occurred following the application of a field with a negative polarity to the semiconductor is also striking (Fig. 3*a*). This result is an argument against the discharge mechanism of the electroadsorption of oxygen, since in a discharge negative charging of the surface is attained after the application of a positive potential to the specimen. However, the data obtained by the field effect method on ZnO single crystals and polycrystalline specimens (with the exception of one study[100] carried out on a ZnO single crystal freshly cleaved in an ultrahigh vacuum at low temperatures) indicate the absence of surface conductivity of the inversion type; the negative charge induced by the electric field increases the conductivity of the specimen by an amount $\Delta\sigma_V$. It has been shown[88] that in an oxygen atmosphere the quantity $\Delta\sigma_V$

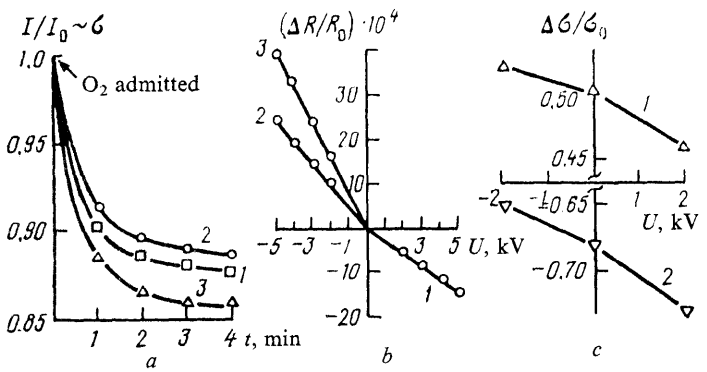


Figure 3. The influence of the field on the adsorption of oxygen and hydrogen on polycrystalline ZnO films. *a*, Variation of the conductivity of the specimen in a stream of the $N_2 + O_2$ mixture: *1*, in the absence of the field; *2*, on application of a field having the – sign to the specimen; *3*, on application of a field having the + sign to the specimen; *b*, The relative changes in resistance $\Delta R/R_0$ as a function of the applied potential: *1*, on application of a field having the – sign to the specimen (the changes $\Delta R/R_0$ *in vacuo* and in a O_2 atmosphere are the same); *2*, on application of a field having the + sign to the specimen *in vacuo*; *3*, ditto in a O_2 atmosphere ($p_{O_2} = 1.3 \times 10^2$ Pa); *c*, the relative changes in the conductivity of the film $\Delta\sigma/\sigma_0$ in the adsorption of hydrogen (curve *1*) and oxygen (curve *2*) atoms as a function of the magnitude and sign of the potential applied to the field electrode ($p_{O_2} = p_{H_2} = 1.33$ Pa).

diminishes (whilst retaining the positive sign) as a result of the additional capture of electrons by the oxygen-generated acceptor traps. The increase in the resistance of the ZnO films when a negative-polarity field is applied to the semiconductor is apparently associated with some kind of additional mechanism of capture of free carriers by the adsorbed oxygen.

The field effect is usually considered in the literature from the standpoint of the breakdown of the electronic equilibrium between the surface and the bulk of the semiconductor when a transverse electric field is applied. However, under conditions where a field acts on defective structures such as those of polycrystalline oxide films, there is apparently a shift of not only the electronic but also of the electronic-ionic equilibrium in the surface region of the semiconductor. In particular, on reduced ZnO films with a high concentration of interstitial Zn^+ ions, there is a possibility of the relaxation polarisation of the specimen under the influence of the external field penetrating the specimen over a distance equal to the Debye shielding length. The characteristic features of the variation of the electrical conductivity of ZnO following the adsorption of oxygen have been explained by the migration of the interstitial zinc in the region of the space charge.[101] In another study,[102] this phenomenon was regarded as an additional mechanism for the discharge of a surface subjected to the action of a corona discharge. The relaxation polarisation of ZnO following the application of a positive potential to the field electrode of the condenser (Fig. 1*c*) should lead to the diffusion of Zn^+ into the bulk of the specimen and of electrons to the ZnO surface. The increase in the resistance of the film observed in electroadsorption of O_2 can be explained by the capture of these electrons by the chemisorbed oxygen.[48]

The relaxation polarisation of the film in an external field apparently determines the mechanism of the electroadsorption of O_2, which has been observed[56] from the additional increase in the resistance of the ZnO film in a O_2 atmosphere following the application of a positive-polarity field to the specimen (Fig. 3*b*), which seemingly conflicts with the ideas of the electronic theory of adsorption. ZnO films with a thickness of (3–5) $\times$ 10^4 nm, comparable to the Debye shielding length, and the condenser illustrated in Fig. 1*f* were used in the above study. The authors suggest that oxygen is adsorbed mainly on the outer side of the film adjoining the gas phase and explain the observed effect by a change in the potential within the Zn film as a result of the accumulation of electrons at the oxide film–gas interface. The mechanism of such electron accumulation is apparently associated with the migration of mobile interstitial zinc ions Zn^+ to the glass–semiconductor interface when a negative potential is applied to the field electrode.

A somewhat different result was obtained on ZnO films 5×10^3 nm thick, sputtered onto a mica support (the condenser illustrated in Fig. 1*b* was used) under conditions where there was no field over the semiconductor surface.[50] The character of the change in the film resistance agrees with the electronic theory of adsorption: the negative-polarity field applied to the semiconductor increases the concentration of negatively charged adsorbed oxygen atoms and reduces the degree of adsorption of positively charged hydrogen atoms (Fig. 3*c*), the relative increase in the concentration of the charged forms of the chemisorbed species amounting to 7–9%. In the study of Ryl'tsev et al.,[50] the electroadsorption effects were investigated at the field-induced charge concentrations $e\Delta n_V$ = 1.6×10^{16} el. charge m^{-2}, which are the maximum possible in the field effect method, whereas in other investigations[48,56] these concentrations were lower by 2–3 orders of magnitude. The shift of the Fermi level, estimated with the aid of Eqn. (7), is $\sim 1.6 \times 10^{-2}$ eV and the values of ΔN^- observed by Ryl'tsev et al.[50] do not exceed those calculated by Eqn. (1).

Consequently the influence of the field on adsorption processes, investigated by Ryl'tsev et al.,[50] is probably due to the "collective" factor. The discrepancy between the results obtained in the above studies[50,56] can be accounted for bearing in mind that Ryl'tsev et al.[50] used several times thinner films, which were "transparent" to the gas, on which adsorption occurred not only on the outer side but also over the entire surface of crystallites, including the space charge region modified by the external field. Furthermore, relaxation polarisation should influence to a lesser extent the results obtained by Ryl'tsev et al.[50] because they used films characterised by a narrow space charge region whose specific resistance was lower by 2–3 orders of magnitude than that of the films used by Constantinescu et al.[56]

The adsorption of atomic hydrogen and oxygen on ZnO[50] and TiO_2 [51] films deposited on quartz supports and subjected to a thermal field treatment has also been investigated. Despite the sevenfold enrichment of the TiO_2 specimen in electrons, the effects observed[51] were small: the rate of adsorption of oxygen atoms increased by 15% and the rate of adsorption of hydrogen atoms diminished by 25%. The authors explained the appreciable change in the conductivity of the semiconductor films after they have been acted upon by a field with a strength of 5×10^6 V m^{-1} at 500–650 K by the electret state of the quartz support. However, according to Kovalenko's data,[103] quartz does not possess the properties of a very effective electret, its surface charge amounting to 5×10^{14} el. charge m^{-2}, which cannot ensure a change in the resistance of the oxide films by an order of magnitude. The type of spectroscopic composition of the quartz was not indicated in the above studies[50,51] and no data were given concerning the electret charging and discharging processes, which precludes a definite conclusion about the mechanism of the action of the field on the electrical conductivity and chemisorption properties of the films.

(c) The desorption of gases by the field using a metal–dielectric–semiconductor system

One of the difficulties in the interpretation of the electroadsorption effects observed from the change in the resistance of the specimen as a result of the action of the field in a gas atmosphere is associated with the impossibility of separating the charges captured by the adsorbed molecules and by the "slow" surface states of non-adsorption origin, whose electrophysical parameters change as a result of adsorption. Studies in which electroadsorption was observed directly by the manometric method are therefore of great interest.[18,52–54] The shift of the adsorption equilibrium after the application of the field was first investigated on polycrystalline *p*-type germanium films $\sim 10^3$ nm thick.[18,52] The condenser illustrated in Fig. 1*b*, with the maximum values E_{max} = 7×10^7 V m^{-1} and $e\Delta n_V = 4 \times 10^{15}$ el. charge m^{-2}, was used in the investigation. The desorption of H_2, CO, and hydrocarbons was observed after the application of a positive-polarity field to the germanium film; the amount of desorbed gas corresponds to thousandths of a monolayer. The application of a field having the opposite sign did not result in the observation of the electrodesorption effect. The authors explain the results[18,52] by a change in the occupancy by electrons of the adsorption centres located on the outer side of the film, directed towards the gas phase, when the field is applied to the inner side. Theoretically this is possible if the film thickness d is smaller than the Debye shielding length L;[72]

according to the authors,[18,52] this conditions holds for $d \simeq 10^3$ nm. The electrophysical parameters of the germanium films used were not indicated in the above studies,[18,52] but according to other data[104,105] thin ($< 10^4$ nm) germanium films have *p*-type conductivity and a high concentration of free carriers [$n_p = (6\text{–}8) \times 10^{24}$ m^{-3}] regardless of the type of conductivity of the single crystal used for the sputtering, which is due[105] to the high density of surface acceptor states. However, in this case $L = 10^2$ nm according to Eqn. (5) and the condition $d < L$ cannot be fulfilled.

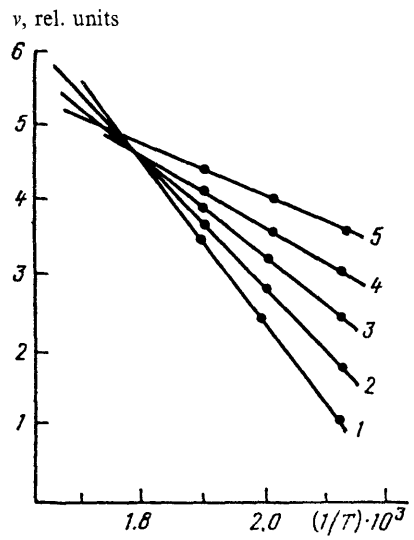


Figure 4. The Arrhenius relations for the rate of decomposition of formic acid at different currents flowing through the Ni–Al_2O_3–Au structure; *i*(A): *1*, 0; *2*, 0.25; *3*, 0.5; *4*, 1.0; *5*, 1.5.

The influence of the field on the desorption of gases as well as catalytic reactions has also been observed in other systems metal–dielectric–thin film involving a semiconductor or a metallic catalyst, but this happened after the application of a field of only one sign, namely one with a positive polarity, to the catalyst.[53–55,106] An appreciable increase in the steady-state rate of decomposition of formic acid and ammonia and also a change in the selectivity of the oxidation of propene on a gold film deposited on a nickel disc with an intervening Al_2O_3 layer has been observed[55] after the application of a negative potential to the nickel disc which performed the role of a field electrode (the condenser illustrated in Fig. 1*b* was used). For different currents flowing through the metal–oxide–metal (MOM) structure, a compensation effect was observed: with increase in temperature, the influence of the field on the rate of decomposition of formic acid was weakened (Fig. 4). The authors[55] explain these results by a change in the rates of the elementary processes in the interaction of the surface compounds with the stream of "hot" electrons arising in the MOM and MDS (metal–dielectric–semiconductor) structures when the electron gas in the dielectric is heated by a strong electric field.[107]

Various mechanisms for the scattering of the kinetic energy of electrons by the surface of the solid and the species adsorbed on it have been detected by the spectroscopy of the characteristic losses of low energy electrons (EELS).[108] The possibility of the vibrational excitation of the molecules adsorbed on the surface of a solid in processes involving the capture of free carriers by deep electron traps has been demonstrated.[109] The resonance adsorption of the excess kinetic energy of the "hot" electrons during scattering by surface states of adsorption origin can apparently be accompanied by both desorption and by the appearance of chemically active species. After the electrodesorption of H_2 and switching off the field at room temperature, the sorption of oxygen and the evolution of methane on germanium films were observed, which may be associated with the activation of the surface hydrocarbon compounds. Unfortunately the leakage currents in the condenser and their dependence on the electric field strength were not indicated in the above studies,[18,52] which makes it difficult to discuss the mechanism of the effect of the field.

(d) Gravimetric study of the influence of the field on the adsorption of oxygen and methanol on a silver catalyst

In order to test the proposed electronic mechanism of the oxidation of methanol, the influence of the field on the adsorption of oxygen and methanol on a silver catalyst coated by an oxide film was investigated gravimetrically[73] at $T = 723$ K and $P = 10^5$ Pa. A result discouraging from the standpoint of the electronic theory was obtained—oxygen was adsorbed for both negative and positive polarity of the external field on the catalyst. A similar result had been obtained earlier[48] on ZnO films using a plane-parallel condenser (Fig. 1*c*). When a field increasing the concentration of electrons in the semiconductor was switched on, the gas pressure in the system fell, which indicated additional adsorption of O_2. When a field with the opposite polarity was switched on, increasing the concentration of holes in the semiconductor, the desorption of oxygen was observed initially at low field strengths, changing subsequently to the adsorption of O_2 with increase in field strength. These results indicate that vacuum insulation conditions are maintained for the mica-free condensers used by Hoenig and Lane,[48] since the occurrence of a gas discharge should have been accompanied only by an increase in pressure.

The fact that the concentration of oxygen adsorbed due to the effect of the field (N-N_0) exceeds by several orders of magnitude the concentration of the induced charge $e\Delta n_V$ is striking.[48,73] The quantity N-N_0 calculated[48] from the change in pressure is 10^{17} molecules m^{-2}, whereas $e\Delta n_V = 10^{13}$ el. charge m^{-2}. The adsorption of oxygen under the influence of fields of both polarities has been explained[72] by the polarisation of non-polar O_2 molecules and the attraction of the induced dipoles to the surface of the cylindrical electrode. An electrostatic mechanism of the field effect on adsorption can also be proposed to account for the results of Hoenig and Lane[48] bearing in mind that the strength of the inhomogeneous electric field near the catalyst greatly exceeds the value calculated from the geometry of the condenser because of the roughness of the surface and is defined by the relation $E = U/Ar$,[9] where U is the external potential difference and r is the radius of individual crystallites or surface rugosities. For $U = 500$V and $r = 10^3$ nm, the energy imparted by the field to the polarised O_2 molecules exceeds their average kinetic energy in the absence of the field. As a result of this, the gas pressure in the inhomogeneous field over the catalyst surface and the degree of coverage of the latter by the adsorbate increase when an external potential is applied.

In the case of polar methanol molecules, the electroadsorption effect has different signs for different polarities of the external field in contrast to oxygen.[73] In a negative-polarity field on a silver catalyst, the degree of coverage by adsorbed methanol increases by 50%, while in a positive-polarity field it diminishes by approximately the same amount. Bearing in mind the clear discrepancy between the low field-induced charges ($e\Delta n_V = 10^{12}$ el. charge m^{-2}) and the large electroadsorption effect, the electroadsorption of methanol, like that of oxygen, must be explained by the electrostatic attraction of the dipolar alcohol molecules to the surface of the charged catalyst and not by the influence of the electronic factor. The orientation of the methanol molecules with the positive end towards the surface (the "hydrogen" orientation) apparently promotes the formation of various surface compounds of methanol, which have been detected by IR spectroscopy.[110] The increase in the partial pressure of the molecules with the "hydrogen" orientation both as a consequence of the dipolar polarisation and the attraction of the dipoles in the inhomogeneous field explains the increase in the amount of adsorbed gas in the presence of a negative-polarity field on a silver catalyst.

4. The influence of the field on catalytic reactions

Examination of the experimental data for the influence of the field on the adsorption of O_2, H_2, and methanol and water vapours on semiconductor adsorbents has shown that in some cases the observed effects can be explained by a shift of the Fermi level and a change in the concentration of free carriers under the influence of the external electric field, while in others they can be explained by secondary effects such as the relaxation polarisation of the solid and the polarisation of the gas in the vicinity of the catalyst surface. A secondary process of this kind must be taken into account also in the interpretation of the results obtained in the study of the influence of the field on the reactions occurring on semiconductors.

a) Dehydrogenation of ethanol on ZnO and the oxidation of methanol on a silver catalyst

In the study of catalytic reactions in the presence of an external field, cylindrical condensers with an air gap and a low field strength E between the plates are most often used. An exception is the study of Ivankiv et al.,[49] where a plane-parallel condenser with a mica plate, illustrated in Fig. 1*c*, permitting the attainment of $E_{max} = 3.5 \times 10^7$ V m^{-1} and $E\Delta n_V = 10^{15}$ el. charge m^{-2}, was used to investigate the influence of the field on the dehydrogenation of ethanol. The study was performed at 523 K on pressed and polished discs prepared from ZnO + 1% CuO powder. Copper oxide is apparently added to achieve a satisfactory conductivity and catalytic activity of the specimens. When a positive-polarity field was switched on, the rate of dehydrogenation of ethanol increased on the catalyst and the yield of aldehyde rose, while for a negative polarity the rate of reaction fell. The authors attribute these effects to a change in the concentration of the electron and hole gas on the surface of the semiconductor when a transverse electric field is applied. The results obtained agree with the idea that electron-accepting surface centres participate in the alcohol dehydrogenation reaction.[111] It is noteworthy that the curve relating the electrocatalytic effects to the electric field strength obtained in the above study[49] reaches a plateau (saturation) at $E = 1.5 \times 10^7$ V m^{-1} and does not change when E is increased to 3×10^7 V m^{-1}. The insignificant leakage currents (3×10^{14} electrons s^{-1}) when the rate of the catalytic reaction in the presence of the field changes (2×10^{17} molecules s^{-1}) is also evidence against a discharge mechanism of the electrocatalytic effect.

The influence of the field on the selectivity of the oxidation of methanol on a silver catalyst covered by an oxide film has been observed[74] at $T = 750$ K and very low concentrations of the field-induced charge ($e\Delta n_V = 10^{12}$ el. charge m^{-2} is smaller by three orders of magnitude than in the study of Ivankiv et al.[49]). A condenser with a cooled field electrode, illustrated in Fig. 1*g*, was used.[74] When a negative-polarity field was switched on, the yield of formaldehyde on the catalyst increased by 7–8%, while in the presence of a positive-polarity field the yield of formaldehyde fell but that of CO_2—the product of the total oxidation of CH_3OH—increased (Fig. 5). The authors explain the observed effect by a change in the concentration of free carriers on the catalyst surface. However, bearing in mind the very low concentration of the induced carriers and the results for the influence of the field on the adsorption of O_2 and CH_3OH, it would probably be more reasonable to attribute the observed electrocatalytic effects to the different reactivities of the surface compounds formed in the adsorption of methanol, with the "hydrogen" and "oxygen" types of orientation, in the partial and total methanol oxidation reactions.

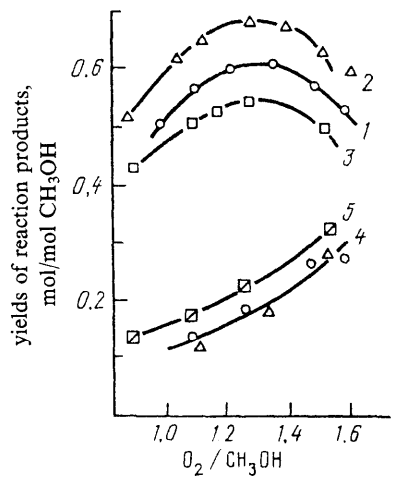


Figure 5. Dependence of the yield of methanol oxidation products on the electric potential applied to the catalyst: *1*, the yield of formaldehyde in the absence of the field; *2*, ditto on application of a field having the – sign to the specimen; *3*, ditto for a field with a + sign applied to the specimens; *4*, the yield of CO_2 in the absence of the field and on application of a field having the + sign to the specimen; *5*, ditto with the – sign of the field applied to the specimen.

(b) The oxidation of CO on NiO, ZnO, and Cu_2O

When different metal oxide films, grown on the surface of a foil by oxidation in oxygen at elevated temperatures were used, a change in the rate of oxidation of CO to CO_2 was observed in the presence of an external electric field.[75–77] In these studies, the external potential was applied between the field electrode and the metallic foil, which ensured the uniformity of the distribution of the potential along the oxide film (the design of the condenser is shown in Fig. 1*h*).

An increase in the rate of oxidation of CO by a factor of 1.5–2 and a decrease in the activation energy for the reaction by 0.21 eV after a positive-polarity field had been applied to the catalyst were observed[75] on nickel oxide obtained by heating nickel foil at 1300 °C in a stream of oxygen. A quantitative comparison of the relative changes in the rate of reaction $\Delta g/g_0$ as a function of the electric field strength, according to Eqns. (2) and (4), has been carried out.[75] Expressing the effective shielding length in terms of a series of semiconductor characteristics of NiO, the authors found that the experimental data agreed quantitatively with the theoretical relation between $\Delta g/g_0$ and E. However, it becomes clear from the comparison of the data presented[75] that the electric field strength in the vacuum gap near the catalyst surface was used as the value of E, whereas Eqn. (4) has been obtained for the electric field strength in the semiconductor at the interface with the vacuum E_n. The quantities E_n and E are linked by the relation $E_n = E/\varepsilon_n$, where ε_n is the dielectric constant of the semiconductor. Bearing in mind that $\varepsilon_{NiO} = 10$ for the field strength $E_{max} = 10^6$ V m^{-1} and $L = 3 \times 10^3$ nm employed,[73] we obtain from Eqn. (4) $V_s V_{s0} = 3 \times 10^{-3}$ eV. The experimentally observed increase in the rate of reaction by a factor of 1.5–2 as well as the decrease in the activation energy for the reaction after the application of the field by 0.21 eV do not correspond to the maximum possible shift of the surface potential, which could also be much smaller as a consequence of the transfer of the charge to surface states.

Deren and Mania[76] studied the influence of the field on the rate of oxidation of CO to CO_2 on the oxide coating of a zinc foil under the conditions of an electrode working in a non-stationary regime, whose activity gradually fell with time. After the application of a positive potential to the field electrode, a sharp increase in the rate of reaction was observed initially, but after several minutes it fell to the value corresponding to the rate of oxidation in the absence of the field. A field with the opposite polarity induces a temporary decrease in the activity of ZnO. These results led to the conclusion that there exists a limiting acceptor stage in the oxidation of CO to CO_2. The increase and then the decrease in the rate of oxidation of CO after the application of a negative-polarity field to the catalyst to values corresponding to a zero external potential is evidence against the discharge mechanism of the electrocatalytic effect. The authors explain the observed time variation by the transfer of the induced electrons to slow surface states.

The electrocatalytic effect occurs also when Cu_2O is used as the catalyst.[77] In order to elucidate the mechanism of the field effect on the catalytic activity of Cu_2O, a study was made of the possibility of the structural modification of the Cu_2O film during its growth on a copper plate at 1050 °C in the presence of a 10^6 V m^{-1} field. When a positive potential was applied to the copper plate, the layer of the Cu_2O scale acquired an increased resistance, in contrast to the copper(I) oxide formed in the absence of the field, which is associated, according to the authors,[77] with the formation of an interstitial solid solution of the excess copper ions. When a field with the opposite polarity was applied, layers of Cu_2O with an excess of oxygen, exhibiting a reduced resistance, were formed. The influence of the field on the oxidation of copper also affects the interplanar spacings in the specimens and the thickness of the oxide films. The copper(I) oxide obtained in the absence and presence of the field exhibited different catalytic properties. The Cu_2O films formed on application of a negative potential to the specimen had an increased activity in the oxidation of CO to CO_2 compared with the films oxidised with application of a positive potential. This difference increased when the reaction was carried out in the presence of a field having the same sign as that used in the formation of the film.

Thus the authors have shown that the enrichment or depletion of the oxide surface in the metal cations under the influence of the electric field may be the cause of the modification of its catalytic activity. A similar change in the defective structure of the surface may occur on NiO and ZnO specimens as a result of the migration of the cations into the region of the space charge modified by the external field. The movement of Ni^{2+} in NiO as well as that of the interstitial zinc in ZnO under conditions where the surface potential is modified by the adsorbed oxygen has been considered.[101,112] It is noteworthy that, when NiO and ZnO films were used as the catalysts, the acceleration of the oxidation of CO to CO_2 was observed for different signs of the external potential: after the application of a positive-polarity field to NiO on a foil and after the application of a negative-polarity field to ZnO. A catalytic study of oxides was carried out in the low-temperature region (180–400 °C), where the CO oxidation reaction probably has an associative mechanism.[113] According to the data of Sokolovskii et al.,[114] the decomposition of surface carbonates on ZnO proceeds with participation of the O_2^- radical-anions. The sharp rise in the catalytic activity of ZnO for a negative potential on the specimen can apparently be explained by the additional adsorption of oxygen in a charged form, which is observed (as described in the previous Section) when the field-induced charge is transferred to the surface adsorption states and also as a consequence of the relaxation polarisation of the oxide in the region of the space charge. According to Gravel',[115] the rate-limiting stage of the oxidation of CO on the NiO catalyst is the interaction of CO_3^- with the adsorbed carbon monoxide. The enrichment of the surface layers of nickel oxide in the Ni^{2+} and Ni^{3+} cations promotes the formation of carbonyl complexes and an increase in the catalytic activity of NiO.

(c) The reversible chemical modification of ZnO, TiO_2, and Pt/TiO_2 film catalysts by the electric field

A series of studies[58–71] have been devoted to the mechanism of the effect of the field on the adsorption and catalytic properties of thin ZnO, TiO_2, and Pt/TiO_2 films deposited on the inner surface of a Pyrex reactor (see the condenser illustrated in Fig. 1*f*). The influence of the field on the rate of decomposition of isopropyl alcohol,[58] the oxidation of CO by NO and O_2,[60] the decomposition of NO[60] and water vapour,[61] and the adsorption of O_2,[59,62] H_2,[61] and CO[62] has been observed. The results have been explained from the standpoint of the electronic theory of catalysis with participation of charged intermediate compounds in the catalytic processes.

In order to test the mechanisms of the field effect, the above reactions were reproduced in a quartz reactor (Fig. 1*f*) and also in experiments using a plane-parallel condenser with a mica plate as the dielectric (Fig. 1*b*). For comparable field-induced charges, the changes in the conductivity of the film ($\Delta\sigma_V$) deposited on mica did not exceed several per cent of the initial conductivity of the specimen, the shift of the Fermi level was less than $0.1kT$, and the influence of the field on the adsorption of oxygen and on the rate of oxidation of CO and of the decomposition of NO were not observed.[57]

In a glass reactor at temperatures in the range 130–160 °C, changes in the conductivity of the ZnO, TiO_2, and Pt/TiO_2 films, which were anomalously high for the field effect method, were obtained for a positive potential applied to the field electrode. For

an initial specific conductance $\sigma_0 = 10^{-11}$–10^{-10} Ω, referred to a unit surface of the specimen, the relative changes $\Delta\sigma_V/\sigma_0$ reached 10^4–10^5 and the activation energy for electrical conduction fell from 0.7–0.9 to 0.1–0.2 eV.[67] The ZnO, Pt/TiO_2, and TiO_2 films retained a low resistance state for several tens of hours after the field had been switched off, exhibiting at the same time a "memory effect" with respect to the action of the field on chemisorption and catalytic processes. However, their transition to the low resistance state was reversible. The application of a negative potential to the field electrode as well as heating to a high temperature resulted in the return of the resistance of the films and of their chemisorption and catalytic properties to the initial values. The results of the measurements of the condenser charging and discharge currents under conditions of the application of fields with the opposite polarity and thermally stimulated depolarisation, also confirming the reversibility of the change in the state of the film catalyst after thermal field treatment, have provided a basis for explaining the observed effects in terms of the relaxation polarisation of the Pyrex glass, which has the properties of a thermoelectret.[63] The thermoelectrisation of the dielectric[116] may be caused both by the formation of dipoles and by the separation of charges in the electret during the migration of current carriers (for example, Na^+ ions in Pyrex glass).

In order to elucidate the possibility of the transfer of sodium from the support to the semiconductor film, the electron diffraction and oxygen absorption methods as well as the method involving the titration of the absorbed oxygen with carbon monoxide were used. It was shown that the passage of a charge through the condenser is accompanied by the electrolytic migration of sodium from the dielectric glass support and its deposition on the surface of a semiconductor film as a finely dispersed metallic phase.[64–66] Thus the earlier results for the influence of the field on adsorption and catalysis can be explained by the surface doping of the oxide films with sodium. The adsorption of oxygen with application of a positive potential to the field electrode takes place as a consequence of the interaction of oxygen with sodium accompanied by the formation of the compounds NaO_2, Na_2O_2, and Na_2O. When sodium superoxide and peroxide are heated, they decompose with evolution of oxygen, the maxima in the thermal desorption spectrum being observed at 370 and 520 K.[65] The decrease in the adsorption capacity of the oxidised TiO_2 film relative to hydrogen after the preliminary application of a positive-polarity field to the field electrode[61] can be explained by the blocking of the hydrogen adsorption centres by sodium atoms.[117] The cause of the evolution of hydrogen when water vapour is admitted into the system after the latter had been exposed to the field is evident:[71] hydrogen is displaced from H_2O by sodium, which binds strongly to the oxygen of the water molecule.

The increase in the rate of absorption of a stoichiometric mixture of O_2 and CO and the simultaneous inhibition of the CO oxidation reaction on ZnO films on application of the field[68] can be explained by the interaction of CO and CO_2 with sodium oxides and the formation of Na_2CO_3. The blocking of part of the ZnO surface by these compounds reduces the steady-state rate of oxidation of CO by a factor of 2–3, while the activation energy and the reaction orders remain unaltered. At the same time, the electrophysical parameters of the ZnO film working under stationary conditions differ greatly from the initial values after the application of the field as a result of the interaction of part of the sodium with the oxygen of the crystal lattice (the activation energy for electrical conduction diminishes from 0.65 to 0.17 eV). Hence it is concluded that the concentration of the conductivity electrons is not the parameter controlling the rate of oxidation of CO on ZnO films.

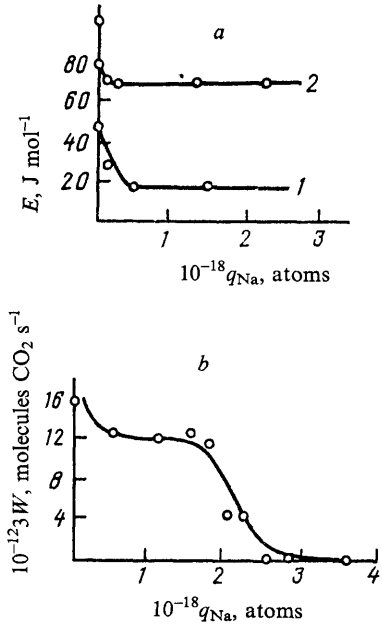


Figure 6. Dependence of the activation energy for electrical conduction in the Pt/TiO_2 film on the amount of Na introduced (*a*) and dependence of the rate of oxidation of CO on the Pt/TiO_2 film (~4 wt.% Pt) on the amount of electrodeposited Na (*b*): *1*, *in vacuo*; *2*, in the presence of the $2CO + O_2$ stoichiometric mixture ($p_{2CO+O_2} = 0.72$ Pa).

In order to elucidate the role of the contact fields between the active phase and the carrier in chemisorption and catalytic processes, the effect of the field on a deposited Pt/TiO_2 catalyst was investigated.[69,70] The transfer of sodium from the support to the surface of the Pt/TiO_2 film is accompanied, as in the case of TiO_2, by a sharp decrease in the activation energy for the electrical conduction of the film at low levels of doping. The activation energy does not change on further increase in the concentration of the added sodium (Fig. 6*a*, curves *1* and *2*). The change in the catalytic properties of the Pt/TiO_2 system on doping with sodium is not correlated with the change in the activation energy for electrical conduction (Fig. 6*b*) and is observed at higher concentrations of added sodium where, according to the conditions in the preparation of the sodium-modified deposited platinum catalyst, the chemical interaction between sodium and platinum becomes possible.[70] This permits the conclusion that the position of the Fermi level in the carrier and the associated contact phenomena at the metal–semiconductor interface do not play an appreciable role in the catalytic process on platinum.

When quartz is used as the dielectric, a similar pattern in the variation of the electrical conductivity and in the catalytic and chemisorption properties of TiO_2 film is observed, but with the

electric field applied at a higher temperature (~530 K) than for Pyrex (430 K), this being associated with the reduced sodium content in quartz.[71]

It is of interest to note that, when a field with a positive polarity is applied to the field electrode during the oxidation of CO to CO_2 on ZnO and Pt/TiO_2 films, the catalysts are not poisoned irreversibly by compounds formed by sodium with O_2, CO, CO_2, and Pt. For standard conditioning at 750 K, these compounds decompose with evolution of CO and CO_2 to the gas phase and the sodium oxide particles remaining on the surface react chemically with the glass, fusing with the latter, as a result of which the catalytic activity of the film returns to its initial value (before the application of the field). The reversible character of the interaction of sodium with the oxides ZnO, TiO_2, and Pt/TiO_2 makes it possible to return the catalytic and adsorption characteristics of these catalysts to the initial values by applying a field with the reverse polarity. This makes it possible to use an external electric field to regulate the rates of catalytic processes in which metallic sodium exhibits a satisfactory activity or is a promoting additive.

At elevated temperatures (from 670 to 720 K), glass begins to play the role of a solid electrolyte and the metal–glass–conducting catalyst film system, in which the metal is exposed to air and the catalyst is placed in the gas investigated, constitutes an electrochemical cell. As a result of adsorption and absorption processes on the metal, glass, and the catalyst, electrode potentials arise between the gas electrodes. They depend on the nature of the catalyst and the gas investigated.[118,119]

The influence of polarisation on the rates of catalytic hydrogen oxidation and ammonia synthesis reactions has been investigated.[120,121]

(d) The influence of an alternating field on the oxidation of CO on NiO and the hydrogenation of ethylene on ZnO

It has been suggested[122] that an alternating external field be used as the basis of a method for the investigation and regulation of heterogeneous catalytic reactions on semiconductors. The possibility of the adsorption of gas molecules for one polarity of the alternating field and of their desorption for the other as a function of the donor–acceptor properties of the gas has been considered.[122] The author[122] called this phenomenon alternosorption. The use of an alternating field makes it possible to control the time during which the species are present on the catalyst surface. Whilst studying the dependence of the rate of reaction on the frequency of the external field, it is possible to determine the optimum time for the elementary step in the oxidation-reduction catalytic process.

The influence of a sinusoidal 2.2×10^6 V m^{-1} external field on the rate of oxidation of CO to CO_2 has been investigated at 123 °C.[123] Nickel discs coated by a layer of NiO 10^3 nm thick, separated from one another by ceramic plates, were used as the catalyst. In the frequency range from 50 to 300 Hz, the rate of oxidation of CO increases severalfold and passes through a maximum located between 100 and 200 Hz. Hence it was concluded that the time during which the adsorbed species are present on the catalyst surface is between 5 and 10 ms.

The influence of the alternating electric field was investigated in greater detail in the hydrogenation of ethylene on a ZnO specimen.[124] A polycrystalline zinc oxide powder was placed between two field electrodes to which an alternating potential was applied (see the condenser illustrated in Fig. 1*d*). When a 1.2×10^5 V m^{-1} sinusoidal potential was switched on in the temperature range from 60° to 146 °C, a change in the reaction orders with respect to hydrogen and ethylene and a decrease in the activation energy from 71 to 48 kJ mol^{-1} were observed. The authors were unable to establish the mechanism of the action of the field, but noted that it may be associated with induction heating or a discharge, because the rate of reaction decreased in the presence of the field.

This study is of interest because of the methodological approach to the selection of the condenser design. A design was selected which does not require specially prepared film catalyst specimens and ohmic terminals on them, the longitudinal alternating field being applied directly to the polycrystalline powdered semiconductor, (Fig. 1*d*). The polycrystalline specimens consisted of a multiplicity of crystallites loosely adjoining one another and having a large number of contacts. The equivalent electric circuit of such specimens consists of a combination of a series of active resistances and capacitances. A theoretical model of the barrier conductivity of polycrystalline films taking into account the change in the filling of the surface states at the boundary between the crystallites, when the height of the barrier was altered by application of an external electric field, was examined.[125] The application of an alternating field to the polycrystalline semiconductor entails an alternation of the charges of the contact capacitances accompanied by the filling and emptying of the surface traps located in the boundary regions of the crystallites.

According to the donor–acceptor mechanism of adsorption and charging, the role of the effective electron and hole traps on the surface of the semiconductor is assumed by electron-accepting and electron-donating centres forming surface complexes with the molecules adsorbed on them. The participation of the main centres and also of the ion pair, consisting of a coordinatively unsaturated cation and an oxygen ion, in the activation of adsorbed ethylene and hydrogen during the hydrogenation of the former was examined by Minachev et al.[126] Apparently the mechanism of the influence of the alternating field on the kinetics of the hydrogenation of ethylene is determined by the change in the filling of these centres by free carriers.

IV. Conclusion

This review has examined studies in which changes were observed in the concentration of the charged form of the chemisorbed species, in the coverage of the surface by the adsorbent, and in the rates of catalytic reactions on application of an electric field at right angles to the surface of the catalyst using various methods: conductimetric, field effect, gravimetric, volumetric, and mass-spectrometric analysis of the gas.

Various designs of the condensers, in which the field strength and hence the charge induced in the semiconductors varied within wide limits (from 10^{12} to 10^{16} el. charge m^{-2}), were used for this purpose. The estimates of the change in the surface potential following the application of the field, obtained in the present review, show that even at the highest concentration of the induced charge, amounting to 10^{16} el. charge m^{-2}, the quantity $V_s - V_{s0}$ on polycrystalline specimens does not exceed tenths of kT. In almost all the studies of the influence of the field on catalytic reactions, the induced charge $e\Delta n_V = 10^{12}$–10^{13} el. charge m^{-2} and the corresponding shifts of the surface potential are negligible ($\ll kT$). Thus, owing to the high density of the surface states, the possibilities of the field effect method for discovering the role of the collective factor in semiconductor catalysis are extremely limited.

The authors explained the results obtained in terms of a change in the filling of the active surface centres by free carriers. Under conditions where almost all the field-induced charge passes to the surface states and the shift of the Fermi level is negligible, the changes in the local properties of the surface under the influence of the captured charge carriers come to the fore. In Vol'kenshtein's theory, the electrons and holes on the semiconductor surface play the role of free valences; their direct involvement in the formation of a bond converts the adsorbed molecules into radicals with an increased reactivity. In the donor–acceptor model of adsorption and charging,[21] the more probable and general case of the deformation of the adsorbed complex in the Coulombic field of the captured charge carrier is considered. This increases the amount of ionic character of the bond and the probability of the dissociation of the molecule. It has been shown[109] that the capture of free carriers by adsorbed states is accompanied by the evolution of the excess energy, which is dissipated in the vibrational modes of the adsorbed molecules, which can also stimulate their dissociation or desorption.

Various secondary effects, i.e. effects not associated directly with a change in the concentration of the free carriers, introduce some uncertainty into the interpretation of the results for the influence of the field on adsorption and catalysis. Essentially, only the change in the chemisorption and catalytic properties of semiconductors following the application of the electric field has been established in the majority of studies, while the question of the mechanism of the action of the field remained open. In the review much attention has therefore been devoted to the most probable mechanisms of chemisorption and catalysis in the presence of the field for the given catalytic systems and associated with the occurrence of a series of physicochemical processes, among which the influence of the relaxation polarisation of the dielectric and of the surface layers of the semiconductor must be specially emphasised.

It is suggested in the electronic theory of catalysis that the field effect method can shift the Fermi level and can alter the concentration of electrons and holes on the semiconductor surface without changing the chemical composition of the catalyst. This point of view is in general incorrect because the application of an external field to defective structures such as polycrystalline semiconductor films and dielectric supports at elevated temperatures (>400 K) is accompanied by the migration of weakly attached ions through space and the establishment of a new electronic–ionic equilibrium. The defective structure and the chemical composition of the catalyst surface are modified as a consequence of this.

It has been established[64–66] that the surface doping of film catalysts with sodium atoms deposited electrolytically from a sodium-containing glass support having the ionic type of conductivity can be achieved with the aid of an external field. The alkali metals sodium and potassium on a carrier exhibit a satisfactory catalytic activity,[127,128] but they are of even greater interest as promoting additives to deposited metallic catalysts.[129,130]

Electrodeposited sodium is introduced onto the surface in the atomic form and exists on it in a finely dispersed metallic state.[65,66] It is of interest to investigate in reducing media the catalytic activity of finely dispersed metallic sodium and of the intermetallic compounds formed when sodium interacts with the active metallic phases of the deposited catalyst. Bearing in mind that, as a consequence of the reversibility of the interaction of sodium with oxides, its surface content can be varied smoothly in either direction and that the amount of electrodeposited metal can be easily evaluated coulometrically, the doping method proposed[64–71] must be recognised as a convenient procedure for the preparation of model film catalysts. The use of other metal-containing glasses makes it possible to extend the class of metallic doping additives.

A series of other physicochemical phenomena, which are apparently responsible for the mechanisms and may be used to regulate adsorption and catalytic processes, have been considered in this review. They include the following.

1. The change in the concentration of polar molecules with a definite type of orientation in strong inhomogeneous local fields near the catalyst surface. The inhomogeneous fields arising as a result of the greater curvature and roughness of the catalyst surface relief may alter both the rate and the selectivity of the catalytic process.

2. The involvement in the catalytic processes of the "hot" electrons arising when a current flows in MOM and MDS structures. As a result of the excess kinetic energy of the "hot" electrons, there is a possibility of the activation of the reactants chemisorbed on the catalyst or of the desorption of the reaction products and hence of the acceleration of the catalytic reaction.

3. The change in the chemical composition of the surface layers of the catalyst in an external electric field. The modification of the defective structure as a result of the increase or decrease in the concentration of cations near the catalyst surface alters the probability of the formation of different surface compounds and can be used in the study of the mechanisms of catalytic processes.

The study of the influence of an alternating field on catalytic reactions is promising. When an alternating field is employed, there is no need to assemble a special condenser, since there are many contact capacitances in the polycrystalline specimen itself at the boundary between the crystallites. When a sinusoidal potential is switched on, the contact capacitances undergo alternating changes in charge and there is a multiplicity of steps involving the capture of free carriers by the surface states arising in the interaction of the adsorbed molecules with the electron-accepting and electron-donating centres on the semiconductor surface, which may entail the deformation of the intramolecular bonds and a change in the reactivity of the adsorbed molecules. Additional physicochemical methods (IR spectroscopy, thermal desorption) can be used to investigate the adsorption and catalytic processes occurring in the presence of an alternating field.

In conclusion one must say that, although the prediction of the electronic theory that the field effect method would prove promising in the study of the elctronic factor in catalysis has not come true, nevertheless an external electric field can be used effectively for the regulation of the chemisorption and catalytic activities of semiconductor catalysts. The different physicochemical processes occurring when an electric field is switched on may stimulate adsorption and catalytic reactions.

References

1. M Ya Fioshin, I A Avrutskaya *Usp. Khim.*, 1975, **44** 2067 [English translation in *Russ. Chem. Rev.*, 1975(11)]
2. R W Murray *Philos. Trans. R. Soc., London, A*, 1981, 302(1468) 2253
3. A M Skudin Elektrokhimiya (Electrochemistry), Izd. VINITI, Moscow, 1982, Vol. 18, p. 228 [Itogi Nauki i Tekhniki (Advances in Science and Engineering)], 1982, **18** 228

4. S D Varfolomeev, I V Berezin Fizicheskaya Khimiya: Sovremennye Problemy (Physical Chemistry: Modern Problems), Izd. Khimiya, Moscow, 1982, p. 68
5. B B Damaskin, O A Petrii, V V Batrakov *Adsorbtsiya Organicheskikh Soedinenii na Elektrodakh* (Adsorption of Organic Compounds on Electrodes), Izd. Nauka, Moscow, 1968, 333 pp
6. V S Bagodskii (Editor) *Problemy Elektrokataliza* (Problems of Electrocatalysis), Izd. Nauka, Moscow, 1980
7. R S Hansen, N C Gardner *Experimental Methods for the Investigation of Catalysis* (Translated into Russian), Izd. Mir, 1972, p. 173
8. A Van Oostrom *Advances in the Study of the Surfaces of Solids* (Translated into Russian), Izd. Mir, Moscow, 1977, p. 40
9. J Block, A W Ganderna *Methods for the Analysis of Surfaces* (Translated into Russian), Izd. Mir, Moscow, 1979, p. 464
10. E Muller *Methods for the Analysis of Surfaces* (Translated into Russian), Izd. Mir, Moscow, 1979, 401
11. F F Vol'kenshtein *Fizikokhimiya Poverkhnosti Poluprovodnikov* (The Physical Chemistry of the Surfaces of Semiconductors), Izd. Nauka, Moscow, 1973, 399 pp
12. K Hauffe *Catalysis. Electronic Phenomena [Reaktionen in und an Festen Stoffen?]* (Translated into Russian) Inostr. Lit., Moscow, 1958, p. 241
13. J E German *J. Chim. Phys.*, 1954, **51** 691
14. S Z Roginskii Poverkhnostnye Svoistva Poluprovodnikov (Surface Properties of Semiconductors), Izd. Akad. Nauk SSSR Moscow, 1962, p. 5
15. O V Krylov *Kataliz Nemetallami* (Catalysis by Non-Metals), Izd. Khimiya, Moscow, 1967, 240 pp
16. N P Keier *Issledovanie Poverkhnosti Katalizatorov Izotopnymi Metodami* (The Study of the Surfaces of Catalysts by Isotopic Methods), Izd. Nauka, Moscow, 1984, 135 p
17. F F Vol'kenshtein *Problemy Kinetiki i Kataliza*, 1955, **8** 201
18. V I Lyashenko, O A Serba, I I Stepko *Dopov. Akad. Nauk Ukr. RSR*, 1962, (3) 350
19. F F Vol'kenshtein *Usp. Khim.*, 1966, **35** 1277 [English translation in *Russ. Chem. Rev.*, 1966(7)]
20. V L Bonch-Bruevich, V B Sandomirskii *Zh. Fiz. Khim.*, 1978, **52** 3009 [English translation in *Russ. J. Phys. Chem.*, 1978(12)]
21. V F Kiselev, O V Krylov *Elektronnye Yavleniya v Adsorbtsii i Katalize na Poluprovodnikakh i Dielektrikakh* (Electronic Phenomena in Adsorption and Catalysis on Semiconductors and Dielectrics), Izd. Nauka, Moscow, 1979, 234 pp
22. J Panciz, I Hasligerova *Collect. Czech. Chem. Commun.*, 1980, **45** 2474
23. E N Korol' (Editor) *Fizicheskie Osnovy Polevoi Mass-Spektroskopii* (The Physical Principles of Field Mass Spectrometry), Izd. Naukova Dumka, Kiev, 1978, p. 82
24. A Bennett *J. Surf. Sci.*, 1975, **50** 77
25. E N Korol, I Yu Posudievsky *Surf. Sci.*, 1986, **169** 104
26. J Block *Chemistry and Physics of Solid Surface. IV* (Springer Series in Chemical Physics). (Edited by R Vanselow, R Howe), Springer Verlag, Berlin etc., 1982, Vol. 20, p. 407
27. B V Il'in *Priroda Adsorbtsionnykh Sil* (The Nature of Adsorption Forces), Gostekhizdat, Moscow–Leningrad, 1952, 124 pp
28. M Domke, J Block, M Drechler *Surf. Sci.*, 1975, **51** 451
29. E V Klimenko, A G Naumovets *Surf. Sci.*, 1969, **14** 141
30. E V Klimenko, A G Naumovets *Fiz. Tverd. Tela*, 1971, **13** 33
31. G Fröhlich *Theory of Dielectrics* (Translated into Russian), Inostr. Lit., Moscow, 1960, 252 pp
32. J Block, B L Moentack *Z. Naturforsch. A*, 1967, **22** 711
33. R Copeland *J. Phys. Chem.*, 1971, **75** 2967
34. A R Anway *J. Chem. Phys.*, 1969, **50** 2012
35. V G Ivanov, T P Smirnova, G N Fursei *Poverkhnost': Fizika Khimiya, Mekhanika*, 1986, (12) 128
36. L N Dobretsov, M V Gomoyunova *Emissionnaya Elektronika* (Emission Electronics), Izd. Nauka, Moscow, 1966, 564 pp
37. D Vladov, Vl Dyakovitch, Sh Dinkov *J. Catal.*, 1966, **5** 412
38. J Block, H Kral *Z. Phys. Chem. (Munich)*, 1960, **24** 66
39. G M Schwab, J Block, G Shultze *Naturwissenschaften*, 1957, **44** 482; *Angew Chem.*, 1959, **71** 101
40. W Pohl, D Warschauer (Editors) *Solids Under High Pressure* (Translation into Russian), Izd. Mir, Moscow, 1966, 524 pp
41. F F Vol'kenshtein, V B Sandomirskii *Dokl. Akad. Nauk SSSR*, 1958, **118** 980
42. V G Baru, F F Vol'kenshtein *Dokl. Akad. Nauk SSSR*, 1966, **167** 1314
43. G K Boreskov *Dokl. Akad. Nauk SSSR*, 1959, **127** 591
44. E P Mikheeva, N P Keier *Kinet. Katal.*, 1964, **5** 748
45. N P Keier, E P Mikheeva *Kinet. Katal.*, 1969, **10** 288
46. E P Mikheeva, N P Keier *Dokl. Akad. Nauk SSSR*, 1974, **218** 906
47. L I Ivankiv, A M Muzychuk *Zh. Fiz. Khim.*, 1968, **42** 424 [English translation in *Russ. J. Phys. Chem.*, 1968(2)]
48. S A Hoenig, J R Lane *Surf. Sci.*, 1968, **11** 163
49. L I Ivankiv, M V Miliyanchuk, A K Filatova *Glubokii Mekhanizm Kataliticheskikh Reaktsii* (Detailed Mechanism of Catalytic Reactions), Izd. Nauka, Moscow, 1968, Vol. 12, p. 327 [Problemy Kinetiki i Kataliza (Problems of Kinetics and Catalysis)]
50. N V Ryl'tsev, E E Gutman, I A Myasnikov *Zh. Fiz. Khim.*, 1981, **55** 986 [English translation in *Russ. J. Phys. Chem.*, 1981(4)]
51. N V Ryl'tsev, I A Myasnikov, E E Gutman *Zh. Fiz. Khim.*, 1983, **57** 381 [English translation in *Russ. J. Phys. Chem.*, 1983(2)]
52. V I Lyashenko, A A Serba, I I Stepko *Kinet. Katal.*, 1966, **7** 1095
53. L I Ivankiv, V V Solyanik *Ukr. Fiz. Zh.*, 1968, **13** 852
54. L I Ivankiv, A M Muzychuk, V V Solyanik *Ukr. Fiz. Zh.*, 1969, **14** 12
55. W Haidinger, J Figer *The Physical Basis for Heterogeneous Catalysis: Proceedings of the 9 Battie Colloquium in the Materials Sciences Held in Gstaad, Sept. 2–6, 1974* (Edited by E Drauglis, R I Jaffee), Plenum Press, New York–London, 1975
56. M Constantinescu, E Segal, M Vass *Rev. Roum. Chim.*, 1976, **21** 503
57. V G Devyatov, E P Mikheeva, L M Usol'tseva *Kinet. Katal.*, 1982, **23** 1022
58. N P Keier, E P Mikheeva, L M Usol'tseva *Dokl. Akad. Nauk SSSR*, 1968, **182** 130
59. N P Keier, E P Mikheeva, L M Usol'tseva *Kinet. Katal.*, 1970, **11** 1009
60. L M Usol'tseva, E P Mikheeva, N P Keier *Kinet. Katal.*, 1973, **14** 1350
61. L M Usol'tseva, E P Mikheeva, N P Keier *Kinet. Katal.*, 1979, **20** 161

62. V G Devjatov, E P Mikheeva, N P Keier *React. Kinet. Catal. Lett.*, 1978, **9** 199
63. E P Mikheeva, V G Devyatov, V M Kolchanova, L M Usol'tseva *Trudy V Sovetsko-Yaponskogo Seminara po Katalizu* (Tashkent, 1979) [Proceedings of the V Soviet–Japanese Seminar on Catalysis (Tashkent, 1979)], Izd. Fan, Tashkent, 1979, p. 188
64. E P Mikheeva, V G Devyatov, V M Kolchanova *Kinet. Katal.*, 1983, **24** 418
65. V M Kolchanova, E P Mikheeva, L M Usol'tseva, et al. *Kinet. Katal.*, 1983, **24** 667
66. V G Devyatov, E P Mikheeva, N P Keier *Kinet. Katal.*, 1983, **24** 671
67. V G Devyatov, V M Kolchanova, E P Mikheeva, L M Usol'tseva *Izv. Akad. Nauk SSSR. Neorg. Mater.*, 1984, **20** 1983
68. V G Devyatov, E P Mikheeva, N P Keier *Kinet. Katal.*, 1984, **25** 239
69. V M Kolchanova, E P Mikheeva *React. Kinet. Catal. Lett.*, 1984, **26** 339
70. V M Kolchanova, E P Mikheeva *React. Kinet. Catal. Lett.*, 1984, **26** 15
71. E P Mikheeva, V G Devyatov, V M Kolchanova *IV Vsesoyuznaya Konferentsiya po Mekhanizmu Kataliticheskikh Reaktsii. Moskva, 1986: Tezisy Dokladov* (The IV All-Union Conference on the Mechanisms of Catalytic Reactions. Moscow, 1986: Abstracts of Reports), Inst. Khim. Fiz. Akad. Nauk SSSR, Moscow, 1986, Part II, p. 406
72. V E Lashkarev *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1952, **16** 203
73. P M Stadnik, V P Fentsik, G K En'ko *Kataliz i Katalizatory*, 1970, **6** 149
74. V P Fentsik, P M Stadnik *Poverkhnostnye i Kontaktnye Yavleniya v Poluprovodnikakh* (Surface and Contact Phenomena in Semiconductors), Izd. Tomsk. Univ., Tomsk, 1964, p. 190
75. J Deren, R Mania *J. Catal.*, 1974, **35** 369
76. J Deren, R Mania *Rocz. Chem.*, 1974, **48** 1565
77. P M Stadnik, S G Kuznetsova *Ukr. Khim. Zh.*, 1970, **36** 117
78. A V Rzhanov *Elektronnye Protsessy na Poverkhnosti Poluprovodnikov* (Electronic Processes on the Surfaces of Semiconductors), Izd. Nauka, Moscow, 1971, 480 pp
79. V I Lyashenko (Editor) *Elektronnye Yavleniya na Poverkhnosti Poluprovodnikov* (Electric Phenomena on the Surfaces of Semiconductors), Izd. Naukova Dumka, Kiev, 1968, 397 pp
80. A Many, G Golstein, N B Grover *Semiconductor Surfaces*, North-Holl. Publ., Amsterdam, 1965, 496 pp
81. S N Kozlov, Yu F Novototskii-Vlasov, V F Kiselev *Fizika i Tekhnika Poluprovodnikov*, 1972, **6** 2102
82. V D Kazarnitskii, S N Kozlov, V F Kiselev, Yu F Novototskii-Vlasov *Dokl. Akad. Nauk SSSR*, 1970, **195** 115
83. A M Murtazin, Yu A Zarif'yants *Fizika i Tekhnika Poluprovodnikov*, 1973, **7** 2041
84. G J Heiland *Phys. Chem. Solids*, 1958, **6** 155
85. G Heiland *Discuss. Faraday Soc.*, 1959, (28) 168
86. H J Krusemeyer *J. Chem. Solids*, 1962, **23** 767
87. H J Krusemeyer *Phys. Rev.*, 1959, **114** 655
88. H J Van Hove *Surf. Sci.*, 1967, **7** 474
89. H J Van Hove *Surf. Sci.*, 1970, **22** 76
90. T I Povkhan *Zh. Nauchn. Prikl. Fotogr. Kinematogr.*, 1974, **19** 221
91. A Many *Crit. Rev. Solid State Sci.*, 1974, **4** 515
92. J Haifdanarson, K Hauffe, J Range *Phys. Status Solidi, A*, 1975, **31** 47
93. G Heiland, D Kohl *Phys. Status Solidi, A*, 1978, **49** 27
94. V F Kiselev *Kompleksoobrazovanie v Katalize* (Complex Formation in Catalysis), Izd. Nauka, Moscow, 1968, Vol. 13, p. 249 [*Problemy Kinetiki i Kataliza* (Prolems of Kinetics and Catalysis)]
95. V F Kiselev *Khemosorbtsiya i Ee Rol' v Katalize* (Chemisorption and Its Role in Catalysis), Izd. Nauka, Moscow, 1970, Vol. 14, p. 25 [*Problemy Kinetiki i Kataliza* (Problems of Kinetics and Catalysis)].
96. V F Kiselev *Dokl. Akad. Nauk SSSR*, 1967, **176** 124
97. V F Kiselev *Kinet. Katal.*, 1970, **11** 403
98. V F Kiselev, V A Matveev, A S Petrov *Kinet. Katal.*, 1980, **21** 523
99. V F Kiselev, V A Matveev *Vestn. Mosk. Univ., Ser. 3: Fizika Astronomiya*, 1985, **26** 82
100. G Heiland *Current Problems in Electrophotography* (Edited by W F Berg, K Hauffe, G de Walter), de Gruyter, Berlin–New York, 1972, p. 73
101. R Glemsa, R J Kokes *J. Phys. Chem.*, 1965, **69** 3254
102. S R Morrison *Current Problems in Electrophotography* (Edited by W F Berg, K Hauffe, G de Walter), de Gruyter, Berlin–New York, 1972, p. 61
103. G M Kovalenko *Kratkie Soobshcheniya po Fizike: Sbornik* (Brief Communications on Physics: Collected Volume), Izd. FIAN, Moscow, 1970, No. 9, p. 15
104. B W Slooper, C O Tiller *J. Appl. Phys.*, 1967, **38** 140
105. R R Humphris, A Catlin *Solid State Electronics*, 1965, **8** 957
106. O S Frolov, O V Snitko, G F Romanova *Ukr. Fiz. Zh.*, 1969, **14** 585
107. M I Elinson (Editor) *Nenakalivuemye Katody* (Non-incandescent Cathodes), Izd. Sov. Radio, Moscow, 1974, p. 69
108. H Lüth *Surf. Sci.*, 1983, **126** 126
109. V F Kiselev, S N Kozlov *Poverkhnost': Fizika, Khimiya, Mekhanika*, 1982, (2) 13
110. A A Davydov *IK-Spektroskopiya v Khimii Poverkhnostnykh Okislov* (IR Spectroscopy in the Chemistry of Surface Oxides), Izd. Nauka, Novosibirsk, 1984, 245 pp
111. V I Yakerson, L I Lafer, A M Rubinshtein *Poverkhnostnye Soedineniya v Geterogennom Katalize* (Surface Compounds in Heterogeneous Catalysis), Izd. Nauka, Moscow, 1975, Vol. 16, p. 49 [*Problemy Kinetiki i Kataliza* (Problems of Kinetics and Catalysis)]
112. R Chrusciel, J Deren, J Nowotny, J Ziolkowski *Bull. Pol. Acad. Sci. Chim.*, 1968, **16** 215
113. G K Boreskov, V I Marshneva *Dokl. Akad. Nauk SSSR*, 1973, **213** 112
114. V D Sokolovskii, G K Boreskov, A A Davydov, et al. *Dokl. Akad. Nauk SSSR*, 1974, **216** 599
115. P Gravel' *Primenenie Teploprovodyashchikh Mikrokalorimetrov v Issledovaniyakh po Geterogennomu Katalizu* (Application of Thermally Conducting Microcalorimeters in Studies on Heterogeneous Catalysis), Inst. Kataliza Sib. Otd. Akad. Nauk SSSR, Novosibirsk, 1973, p. 73
116. G M Sessler *Electrets* (Translated into Russian), Izd. Mir, Moscow, 1983, p. 25 [*Problemy Prikladnoi Fiziki* (Problems in Applied Physics)]
117. N I Pospelova, I V Myasnikov *Dokl. Akad. Nauk SSSR*, **170** 1372

118. A I Krasil'shchikov, L G Antonova, F P Ivanovskii *Kinet. Katal.*, 1960, **1** 210
119. L G Antonova, A I Krasil'shchikov *Glubokii Mekhanizm Kataliticheskikh Reaktsii* (Detailed Mechanisms of Catalytic Reactions), Izd. Nauka, Moscow, 1968, Vol. 12, p. 122 [Problemy Kinetiki i Kataliza (Problems in Kinetics and Catalysis)]
120. A I Krasil'shchikov, L G Antonova *Dokl. Akad. Nauk SSSR*, 1953, **91** 291
121. L M Dmitrienko, S S Laginov, R F Sivyakova *Kinet. Katal.*, 1960, **1** 379
122. E G Rochov *J. Inorg. Nucl. Chem.*, 1967, **29** 65
123. V-J Lee *Science*, 1966, **152** 514
124. R D Williams, S K Sikdar *J. Catal.*, 1975, **38** 147
125. N I Gol'dman, A G Zhdan *Fizika i Tekhnika Poluprovodnikov*, 1976, **10** 1839
126. Kh M Minachev, Yu S Khodakov, V S Nakhshunov *Usp. Khim.*, 1976, **45** 280 [English translation in *Russ. Chem. Rev.*, 1976(2)]
127. US P. 3 222 346
128. D Savoia, E Tagliavini, C Trombini, A Umani-Ronchi *J. Organomet. Chem.*, 1981, **204**(3) 281
129. A Ozaki, K Aika *Problems of Nitrogen Fixation* (Translated into Russian), Izd. Mir, Moscow, 1982, p. 213
130. R D Conzalez, H Miura *J. Catal.*, 1982, 77(2) 338