BOUND STATES IN CATALYSIS: NEW ELECTRODYNAMICAL AND QUANTUM CHEMICAL MODELS IN ELECTRON THEORY OF CATALYSIS

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New approach in the electron theory of catalysis, based on the electrodynamical and quantum-chemical modelling of catalytic processes in metallic materials is developed. We have determined and studied the electron structure parameters of metal alloys which determine the catalytic activity of metallic alloys for the simple model reaction of the type: $H = H^+ + e$ and $O_2^- = O_2 + e^-$. It has been quantitatively shown how the Fermi level position dependence upon the metal alloys components concentration influences on the catalytic activity of alloys.

1. Investigation of the catalytic activity for metals and metal alloys and development of a comprehensive theory for catalysis is one of the most important problems. Its solution is of great importance, for example, under creation and carrying out the electrochemical generators etc. [1–12]. It is known that variation of component concentration in a metallic alloy can result in the corresponding change of its both catalytic activity and electrochemical properties. The attempts of comprehensive quantitative description of the electron structure of metals (metallic alloys) in the processes on electrodes of electrochemical generators have been undertaken in a whole number of papers [1-3], in particular, within the conceptual models with the use of the density functional formalism [3]. In these quite effective (from the point of view of calculations) models the description is made in terms of electron density at the metal or alloy surface. As a result, these models are not enough sensitive to the value and the density of states at the Fermi surface. Evidently, in a great number of papers [1–3]

the catalysis and hemosorption problems are considered within ab initio quantum chemistry methods. Naturally, such quantum-chemical calculations give very useful information about the processes considered, however some quite important moments of physical and chemical nature of these processes often remain to the certain extent veiled. As an alternative, one can consider effective approaches, developed on the basis of both electrodynamical and quantum-chemical modeling [4–6]. Here we develop a new model approach to determine the catalytic activity of binary metallic alloys. The electron structure parameters of metal alloys which determine the catalytic activity of metallic alloys to the simple model $H = H^+ + e$ or $O_2^- = O_2 + e^-$ -type reaction, are considered.

2. The electron structure of a metallic system can be approximated by a set of isotropic s-d bands [4, 5]. The static dielectric permeability is represented as follows:

$$\varepsilon = 1 + \varepsilon_{ss} + \varepsilon_{dd} + \varepsilon_{sd} + \varepsilon_{ds}, \quad (1)$$

where ε_{ij} describes the contribution due to the *i-j* transitions into ε. In the free-electron

approximation the expression for ε_{ss} is given by

$$\varepsilon_{ss} = 2\pi v_s (E_F) k^{-2} \{1 + [4(k_F^s)^2 - k^2] Ln |(2k_F^s + k)/2k_F^s - k)|/4k_F^s k\} \quad \text{.................(2)}$$

where $k = q\, a_B$; q is wave number; a_B – Bohr radius; $q_F = (3\pi^2\, z_i\, /\Omega)^{1/3}$; z_i – the number of electrons in the *i*-th band; $v_i(E_F) = N_i(E_F) a_B^2 e^e$, $N_i(E_F)$ – the density

of states at the Fermi surface in the *i*-th band. The corresponding expression for ε_{dd} has the following form:

$$\varepsilon_{dd} = 2\pi v_d (E_F) k^{-2} |M_{dd}|^2 \{1 + [4(k_F^d)^2 - k^2] Ln |(2k_F^d + k)/2k_F^d - k)|/4k_F^d k\} \quad \text{........(3)}$$

Here the matrix element M_{dd} is determined by the superposition of the wave functions for d electrons. The contribution $\varepsilon(ds)$ is important only for the systems containing noble metals . This contribution is determined as follows:

$$\varepsilon_{ds} = [2m_s k_d e^2 f_c /\pi h^2 k^2]\{1 + [4(k_d)^2 - k^2] Ln |(2k_d + k)/2k_d - k)|/4k_d k\} \quad \text{...............(4)}$$

where *m(s)* is the effective mass of electron in the conduction band; k_d, f_c- numeric parameters [6]. Note that the contribution of ε_{ds} in (1) for transition metals is about several percents. The effective potential, which imitates the effect of the potential metal (metal alloy) field on the inculcated hydrogen atom, is determined as follows:

$$\Phi(r) = -\frac{2e^2}{\pi r} \int_0^\infty \frac{\sin kr}{k\varepsilon(k)} dk \quad . \qquad (5)$$

It is supposed that the task considered has the spherical symmetry and the crystal potential is fully screened by the conductivity electrons. Substitution of (1) to (5) leads to the following expression:

$$\Phi(r) = -e^2\, a/r\, \exp[-\alpha R]\cos[\alpha R] \ . \qquad (6)$$

Here

$$\alpha = [\pi^{-1} 12(k_F^s)^2]^{-1/4} \{v_s(E_F) + (k_F^d/k_F^s)v_d(E_F) + $$
$$+ f_c(k_F^d/k_F^s)^2 v_s(E_F)\}^{1/4}$$

$$R = 2q_F^s r \qquad a = (k_F^s)^{-1}$$

The numeric solution of the Schrödinger equation [9, 10] for hydrogen atom in the potential field $\Phi(r)$ gives the corresponding spectrum of states, which can be continuous or discrete depending upon the parameter $\zeta^{-1} = \alpha/a$. The spectrum is continuous if $\zeta < \zeta_0 = 0.362$ (the corresponding material is a good catalyst for the hydrogen ionization reaction); if $\zeta > \zeta_0$, then the spectrum is discrete (the metal is not a catalyst for the reaction in question).

In the binary metallic alloy both the Fermi level position E_F and the corresponding density of states $v(E_F)$, and, hence, the electron structure parameters α and a vary with the admixture concentration c. For approximate account of the given variation it is possible to use the Thomas-Fermi approach [3]. Suppose the admixture atoms to form a sphere. The radius is related to the concentration as $(qRc)^{-3} = (qr_s)^{-3}c$ (r_s – the characteristic parameter of electron gas). For

the screened potential $V(r)$ near the admixture (under condition: $|\Delta E_F - V| < E_F$), the corresponding Poisson equation is as follows:

$$\Delta V(r) = q^2 \{ V(r) - \Delta E_F \}. \quad (7)$$

The elementary solution of equation (7) under the boundary conditions: $(dV/dr)_{Rc}=0$, $V(Rc)=0$, $V \to - Z_v e /r$, $r \to 0$ (Z_v is the difference of the component valences) has the form

$$V(r, R_c) - \Delta E_F = [-Z_v e /r]\{qR_c ch[q(R_c - r)] + sh[q(R_c - r)]\}/[qR_c ch(qR_c) + sh(qR_c)]. \quad (8)$$

The second boundary condition provides the expression for the Fermi level shift depending upon the concentration c:

$$\Delta E_F = Z_v e^2 q /[qR_c ch(qR_c) + sh(qR_c)]. \quad (9)$$

One can see that for a binary alloy the value $v(E_F)$ is substituted by the value $v(E_F) = v(E_F) + \Delta v(E_F)$. The parameters, which determine the catalytic activity for metallic compounds, are directly dependent on the component concentration. As an example, we estimate the catalytic activity of Ni-Cu compound for the reaction $H = H^+ + e$. The calculations show that the compound with the concentration of Cu ≤ 15% is an effective catalyst for the cited reaction, however with the growth $\xi(\xi \to \xi_0)$ the situation changes into opposite in accordance with the experimental data.

In the case of the model reaction of $O_2^- = O_2 + e^-$ type the situation is inverse in comparison with the above described one. The numeric solution of the Schrödinger equation [11, 12] for oxygen molecule in the potential field $\Phi(r)$ gives the corresponding spectrum of the states, which can be continuous or discrete depending on the parameter $\zeta^{-1} = \alpha / a$. The spectrum is continuous if $\zeta > \zeta_{bound}$ (the corresponding material is a good catalyst for the studied reaction). If $\zeta < \zeta_{bound}$, then the spectrum is discrete (the material is not a catalyst). Some

promising catalytic materials and their catalytic activity predictions for some materials (transition metals and alloys, semiconductors, lanthanides, perovskites) were considered within developed approach [12–17].

In conclusion we emphasize that here we concentrate our attention on the principal ideas. We believe that the proposed approach can be improved by the account of the whole number of additional factors (the electrolyte influence, surface effects, electrode potential, the electrolyte type, the concentration of electrons in the layer etc. [16,17]). Especially interesting is the development of similar models for semiconductors and for other reactions (especially important are catalytic processes for industry).

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ЗВ'ЯЗАНІ СТАНИ В КАТАЛІЗІ: НОВІ ЕЛЕКТРОДИНАМІЧНА ТА КВАНТОВО-ХІМІЧНА МОДЕЛІ В ЕЛЕКТРОННІЙ ТЕОРІЇ КАТАЛІЗУ

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