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SURFACE STATES AND ACTIVITY OF NANOCATALYST: ZERO-RANGE POTENTIALS MODEL

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Abstract

We investigate the problem of nanocatalysts improvement. Namely, the increase of the catalytic activity due to irregular inclusion at the nanoparticle surface is under consideration. A 3D model of a half-crystal with irregular impurities at the surface is suggested. It is shown that the surface impurities lead to the appearance of surface bound states or surface bands which give rise to the electron density at the surface related with the catalytic activity. The suggested solvable model is based on the theory of self-adjoint extensions of symmetric operators.

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1 Introduction

Nano catalysts are widely used in modern chemistry due to high surface/volume ratio for nanoparticles (see, e.g., [1]). High catalytic activity and, at the same time, thermal stability of nano catalysts are observed also due to unusual behavior of the nanoparticles in the matrix [2]. Peculiarities of nanoparticles and nanocomposite structures lead to changes of the catalysts properties (see, e.g., [3] - [12]). One can mention an interesting phenomenon: the catalytic activity of nanocatalyst increases considerably if there are irregular inclusions at the nanoparticle surface. It can be related with the change of surface electron states. There are different (rather complicated) approaches (see, e.g.. [13]) for the description of these catalysts. It is also worth constructing simple models which allows one to explain and predict the properties of the system. In this paper we suggest a 3D model which shows that the effect of increasing the surface electron density (and, correspondingly, the catalytic activity) can be related with the surface irregular

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inclusion. A simple and rough variant (1D model) for the explanation of this phenomenon was suggested in [14]. It was discussed in [15].

To construct a model of half-crystal we use zero-range potentials. Introducing such potential, really, reduces to a "boundary" condition (more precisely, given logarithmic derivative) at the chosen point x_0:

$$\frac{1}{r\psi}\frac{\partial(r\psi)}{\partial r} \to \alpha, \quad r \to 0.$$

Here r is the distance from x_0. Correct mathematical description for this procedure is given in the framework of operator extensions theory (see, e.g., [16] and references in [17]). Namely, one starts from the self-adjoint Laplacian in $L_2(\mathbb{R}^3)$ with the domain $W_2^2(\mathbb{R}^3)$. The closure of its restriction on the set of smooth functions vanishing at x_0 is a symmetric operator with the deficiency indices $(1,1)$. It has one-parameter (α) family of self-adjoint extensions which give us the model operators with the point-like potential.

Nanoparticle can be considered as a half-crystal with impurities at its surface. First, consider 3D half-crystal. Introduce some notations. Let $\Lambda_2^{n_1}$ be a two-dimensional lattice:

$$\Lambda_2^{n_1} = \{n_1 a_1 + n_2 a_2 + n_3 a_3 \in \mathbb{R}^3 | (n_2, n_3) \in \mathbb{Z}^2, n_1 \in \mathbb{N} \cup 0\},$$

where a_1, a_2, a_3 are basic lattice vectors, $\Gamma_2^{n_1}$ be the dual lattice:

$$\Gamma_2^{n_1} = \{n_1 b_1 + n_2 b_2 + n_3 b_3 \in \mathbb{R}^3 | (n_2, n_3) \in \mathbb{Z}^2, n_1 \in \mathbb{N} \cup 0\},$$

where b_1, b_2, b_3 satisfy the condition $b_j \cdot a_n = 2\pi\delta_{jn}$. We denote the Brillouin zone by $\hat{\Lambda}_2^{n_1}$):

$$\hat{\Lambda}_2^{n_1} = \{s_2 b_2 + s_3 b_3 \in \mathbb{R}^3 | s_j \in [-1/2, 1/2), j = 2, 3\},$$
$$\hat{\Gamma}_2^{n_1} = \{s_2 a_2 + s_3 a_3 \in \mathbb{R}^3 | s_j \in [-1/2, 1/2), j = 2, 3\}.$$

We consider zero-range potential lattice. These potentials are introduced as it has been described above. Taking into account the periodicity, we use Bloch's condition. In this case the Green function $G_c(x, y, k)$ for the half-crystal can be obtained using the Poisson summation formula [16]. Let

$$S(x, \theta, k) = \sum_{\lambda \in \Lambda_2^0, \lambda \neq x} \frac{e^{ik|\lambda - x|}}{4\pi|\lambda - x|} e^{-i\lambda\theta}.$$

Then,

$$S(x, \theta, k) = |\hat{\Gamma}_2^0|^{-1} \sum_{\gamma \in \Gamma_2} \frac{e^{-\sqrt{|\gamma+\theta|^2 - k^2}|x^1|}}{2\sqrt{|\gamma + \theta|^2 - k^2}} e^{-i(\gamma+\theta)\tilde{x}}, \tag{1}$$

for $x = (x^1, \tilde{x}) \in \mathbb{R}^3, x^1 \neq 0$;

$$S(x, \theta, k) = |\hat{\Gamma}_2^0|^{-1} \lim_{\omega \to \infty} \sum_{\gamma \in \Gamma_2, |\gamma+\theta| \leq \omega} \frac{e^{-i(\gamma+\theta)\tilde{x}}}{4\pi|\gamma + \theta|} \arctan \frac{|\gamma + \theta|}{ik}, \tag{2}$$

for $x = (0, \tilde{x})$ which does not belong to Λ_2^0;

$$S(x,\theta,k) = e^{-i\theta x}(-\frac{ik}{4\pi} + \lim_{\omega\to\infty}(\sum_{\gamma\in\Gamma_2, |\gamma+\theta|\le\omega} \frac{|\hat{\Lambda}_2^0|}{8\pi^2\sqrt{|\gamma+\theta|^2-k^2}} - 2\pi\omega)), \quad (3)$$

for $x \in \Lambda_2^0$.

The Green function $G_c(x,y,k)$ has the form

$$G_c(x,y,k) = \frac{e^{ik|y-x|}}{4\pi|y-x|} + a_c \sum_{n_1=0}^{+\infty} \sum_{\lambda\in\Lambda_2^{n_1}, \lambda\neq x} \frac{e^{ik|\lambda-x|}}{4\pi|\lambda-x|} e^{-i\lambda\theta}.$$

Coefficient a_c is determined from the condition at a lattice node (e.g., 0):

$$\begin{gathered} a_c = \frac{e^{ik|y|}}{4\pi|y|}(-\alpha + \sum_{n_1=0}^{+\infty} \sum_{\gamma\in\Gamma_2^{n_1}} \frac{(k^2-k_0^2)|\hat{\Gamma}_2^0|^{-1}}{(|\gamma+\theta|^2-k^2)(|\gamma+\theta|^2-k_0^2)} + \\ \frac{1}{4\pi}(\sum_{n_1=0}^{+\infty} \sum_{\lambda\in\Lambda_2^{n_1}, \lambda\neq 0} \frac{e^{ik_0|\lambda|-i\lambda\theta}}{4\pi|\lambda|} - 1))^{-1}. \end{gathered} \quad (4)$$

Here k_0 is some imaginary value ($k_0^2 < 0$). It is a model parameter. α_1 corresponds to the "strength" of the point-like potentials of the lattice. We use the representation of the lattice sum from [18, 19]. Note that the denominator $(-\alpha + g_k(0,\theta))$ of the right hand side of (4) has the following properties:

it is meromorphic as a function of $k*2$ with simple poles at $k^2 = |\gamma+\theta|^2, \gamma \in \Gamma$;

$\overline{g_{\overline{k}}(0,\theta)} = g_k(0,\theta)$;

it is symmetric with respect to each component of the quasi-momentum θ;

at the real axis it is real, it has singularities at $k^2 = |\gamma+\theta|^2, \gamma \in \Gamma$ and between them increase monotonically from $-\infty$ to ∞, moreover, $g_k(0,\theta) \to -\infty$ if $k^2 \to -\infty$.

The behavior of the function $g_k(0,\theta)$ is shown in Fig. 1. The spectral equation is

$$\alpha = g_k(0,\theta).$$

Variation of the quasi-momentum θ leads to the shift of the roots and gives us bands.

2 Model of surface impurity

To construct point-like impurity near the half-crystal surface, we need the Green function for the half-crystal corresponding to a source posed at a point outside the half-space filled by crystal. Let $G_c(x,x_0,k)$ be the Green function for the half-crystal with the source at x_0. To construct the point-like potential at x_0, we, first, restrict the Hamiltonian for the half-crystal on the set of smooth functions vanishing at x_0. The closure of the obtained operator is symmetric (non-self-adjoint) with the deficiency indices $(1,1)$. It's self-adjoint extension gives us the model operator in question. Taking into account the expression

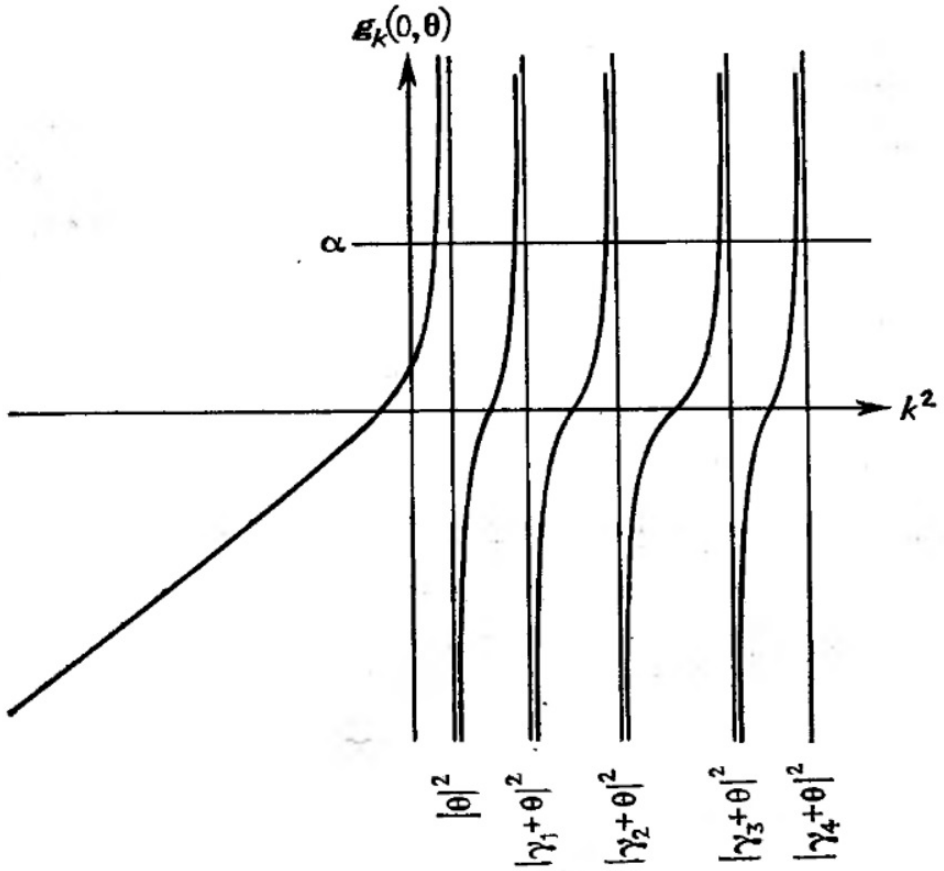

Figure 1: The behavior of the function from the spectral equation. Intersections of the horizontal line with the curves gives one the corresponding point of the spectral band for fixed quasi-momentum θ.

for $G_c(x, x_0, k)$, one can see that the Green function for the model operator has the following form

$$G(x,y,k) = G_c(x,y,k) + a\frac{e^{ik|x_0-x|}}{4\pi|x_0-x|} = \frac{e^{ik|y-x|}}{4\pi|y-x|} + a\frac{e^{ik|x_0-x|}}{4\pi|x_0-x|} + a_c\sum_{n_1=0}^{+\infty}\sum_{\lambda\in\Lambda_2^{n_1},\lambda\neq x}\frac{e^{ik|\lambda-x|}}{4\pi|\lambda-x|}e^{-i\lambda\theta}. \tag{5}$$

Here a_c is determined in (4). a is determined from zero-range potential with the strength α_0 condition at x_0:

$$a = G_c(x_0,y,k)((G_c(x,x_0,k) - G_c(x,x_0,k_0)|_{x=x_0} - \alpha_0)^{-1}.$$

One can see that the appearance of additional point-like potential leads to additional singularity of the Green function in comparison with the singularities of $G_c(x_0, y, k)$ (the singularities give us the spectrum). The spectral equation is as follows

$$(G_c(x,x_0,k) - G_c(x,x_0,k_0)|_{x=x_0} - \alpha_0 = 0.$$

Keeping in mind Fig. 1, one can see that for sufficiently large α_0^{-1} this eigenvalue lies below the continuous spectrum of the half-crystal Hamiltonian. We can mention that the corresponding eigenstate is localized near the potential center, i.e. at the half-crystal surface.

3 Discussion

There is no problem to add a finite number (n) of point-like potentials near the surface. The condition at these points $x_1, x_2, ...x_n$ gives us a system of n linear equations for the corresponding coefficients. The equation for eigenvalues is given by the vanishing of the determinant

$$\det A = 0,$$

$$A_{jj} = G_c(x,x_0,k) - G_c(x,x_0,k_0)|_{x=x_j} - \alpha_j, \quad A_{jp} = G_c(x_j,x_p,k).$$

In general, it leads to n eigenvalues and, correspondingly, to n eigenstates localized near the crystal surface.

Another possibility is to add a layer ($\Lambda_2^{-s_1}$) with characteristics differing from that for the half-crystal, particularly, another distance from the substrate than between the internal layers. The systems with analogous structure (having perturbed monolayer) is used in photonic crystals (see, e.g., [20]). In this case the expression for the Green function (5) is replaced by the following one where one has an additional sum corresponding to the monolayer instead of the term corresponding to the single additional center:

$$G(x,y,k) = G_c(x,y,k) + a\sum_{\lambda\in\Lambda_2^{-s_1},\lambda\neq x}\frac{e^{ik|\lambda-x|}}{4\pi|\lambda-x|}e^{-i\lambda\theta} = \frac{e^{ik|y-x|}}{4\pi|y-x|} + a\sum_{\lambda\in\Lambda_2^{-s_1},\lambda\neq x}\frac{e^{ik|\lambda-x|}}{4\pi|\lambda-x|}e^{-i\lambda\theta} + a_c\sum_{n_1=0}^{+\infty}\sum_{\lambda\in\Lambda_2^{n_1},\lambda\neq x}\frac{e^{ik|\lambda-x|}}{4\pi|\lambda-x|}e^{-i\lambda\theta}. \tag{6}$$

Here s_1 is some positive number, $s_1 \neq 1$, coefficient a is related with the strength of the point-like potentials in added layer (it differs from a_c). The corresponding additional term appears in the spectral equation. It produces a new spectral band ("monolayer band"). This band is shifted with respect to the crystal bands. If s_1 differs sufficiently from 1 and a from a_c then this band is separated from the crystal bands. In this case we have the surface state (surface band) localized in a neighborhood of the added monolayer.

Thus, it is shown that local surface impurities lead to the appearance of bound states localized near the nanoparticle surface. Analogously, a perturbation of the whole surface layer gives us a band state concentrated near the surface. In both cases we have additional electron density near the nanoparticle surface. It results in increasing of the catalytic activity. It correlates with the experimental results concerning nanocatalyst with surface impurities.

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References

[1] Xu, W., Kong, J.S., Chen, P. *Probing the catalytic activity and heterogeneity of Au-nanoparticles at the single-molecule level*, Phys. Chem. Chem. Phys. **11** (2009), 2767-2778.

[2] Al'myasheva, O.V., Vlasov, E.A., Khabenskii, V.B., Gusarov, V.V., *Thermal stability and catalytic properties of the composite amorphous Al_2O_3-nanocrystals ZrO_2*, Russian Journal of Applied Chemistry. **82** (2009), no 2, 217-221 (DOI: 10.1134/S1070427209020104).

[3] Glibin, V., Svirko, L., Bashtan-Kandybovich, I., Karamanev, D., *Synthesis, surface chemistry and electrocatalytic properties of oxygen-modified tungsten carbide in relation to the electrochemical hydrogen oxidation*, Surface Science **604** (2010), 500-507.

[4] Hyman, M.P., Vohs, J.M., *Reaction of ethanol on oxidized and metallic cobalt surfaces*, Surface Science **605** (2011), 383-389.

[5] Weilach, Ch., Spiel, Ch., Fittinger, K., Rupprechter, G., *Carbonate formation on Al2O3 thin film model catalyst supports*, Surface Science **605** (2011), 1500-1506.

[6] Su, Y., Han, S., Zhang, X., et al. *Preparation and visible-light-driven photoelectrocatalytic properties of boron-doped TiO_2 nanotubes*, Mater. Chem. Phys. **110** (2008), no 2-3, 239-246.

[7] Chuasiripattana, K., Warschkow, O., Delley, B., Stampfl, C., *Reaction intermediates of methanol synthesis and the water-gas-shift reaction on the ZnO(0001) surface*, Surface Science **604** (2010), 1742-1751.

[8] Polyakov, E.V., Krasilnikov, V.N., Gyrdasova, O.I., Buldakova, L.Yu., Yanchenko, M.Yu., *Synthesis and photocatalytic activity of quasi-one-dimensional (1-D) solid solutions $Ti_{1-x}M_xO_{2-2x/2}$ (M(III)= Fe(III), Ce(III), Er(III), Tb(III), Eu(III), Nd(III) and Sm(III), $0 \leq x \leq 0.1$)*, Nanosystems: Phys. Chem. Math. **5** (2014), no 4, 553-563.

[9] Gusarov, V.V., Al'myasheva, O.V., Vlasov, E.A., Onufrienko, S.V., Bezlepkin, V.V., Semashko, S.E., Ivkov, I.M., Khabenskij, V.B., Granovskij, V.S., Beshta, S.V. *Passive Catalytic Recombiner of Hidrogen.* The patent of Russian Federation 2360734. Application: 2008127137/04, 23.06.2008, Effective date for property rights: 23.06.2008, Date of publication: 10.07.2009.

[10] Lermontov, S.A., Malkova, A.N., Yurkova, L.L., Baranchikov, A.Ye., Ivanov, V.K., *Sulfated nano-ceria as a catalyst of hex-1-ene oligomerization*, Nanosystems: Physics, Chemistry, Mathematics. **4** (2013), no 5, 690-695.

[11] Almjasheva, O.V., Postnov, A.Yu., Maltseva, N.V., Vlasov, E.A., *Thermostable catalysts for oxidation of hydrogen based on ZrO2-Al2O3 nanocomposite.* Nanosystems: Physics, Chemistry, Mathematics, **3** (2012), no 6, 75-82.

[12] Selvamuthumari, J., Meenakshi, S., Ganesan, M., Nagaraj, S., Pandian, K. *Antibacterial and catalytic properties of silver nanoparticles loaded zeolite: green method for synthesis of silver nanoparticles using lemon juice as reducing agent.* Nanosystems: Physics, Chemistry, Mathematics, **7** (2016), no 4, 768–773.

[13] Erikat, I. A., Hamad, B. A., Khalifeh, J. M., *Catalytic oxidation of CO on Ir(100)*, Physica Status Solidi (b),**248** (2011), no 6, 1425-1430.

[14] Popov, I.Yu., Blinova, I.V., Gusarov, V.V., *A Model of Irregular Impurity at the Surface of Nanoparticle and Catalytic Activity.* Communications in Theoretical Physics, **58** (2012), no 1, 55-58.

[15] Oksengendler, B.L., Askarov, B., Nurgaliyev, I.N., Maksimov, S.E., Nikiforov, V.N. *Nanocatalysis: hypothesis on the action mechanism of gold.* Nanosystems: Physics, Chemistry, Mathematics, **6** (2015), no 2, 249–261.

[16] Albeverio, S.,Gesztesy, F.,Hoegh-Krohn, R., Holden, H., *with an appendix by P.Exner. Solvable Models in Quantum Mechanics*, AMS Chelsea Publishing, Providence, R.I., 2005.

[17] Popov, I.Y., Kurasov, P.A., Naboko, S.N., Kiselev, A.A., Ryzhkov, A.E., Yafyasov, A.M., Miroshnichenko, G.P., Karpeshina, Yu.E., Kruglov, V.I., Pankratova, T.F., Popov, A.I.. *A distinguished mathematical physicist Boris S. Pavlov*. Nanosystems: Physics, Chemistry, Mathematics. **7**, (2016), 782–788.

[18] Karpeshina, Yu.E., *Spectrum and eigenfunctions of Schrödinger operator with zero-range potential of homogeneous lattice type in three-dimensional space*. Theor. Math. Phys., **57** (1983), 1156-1162.

[19] Popov, I. Y., Adamyan, V.M.,Blinova, I.V., Popov, A.I., *Waveguide bands for a system of macromolecules*. Nanosystems: Physics, Chemistry, Mathematics, **6** (2015), no 5, 611-617.

[20] Popov I.Yu., *Zero-range potential model for a waveguides in photonic crystals*. Rep. on Math.Phys., **45** (2000), no 2, 207-216.