A SHELL MODEL FOR QUANTITATIVE XPS ANALYSIS OF SUPPORTED CATALYSTS: SYSTEMS WITH A LOW SPECIFIC SURFACE AREA

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A shell model for quantitative analysis of supported catalysts with a low specific surface area by X-ray photoelectron spectroscopy is developed. A new method for estimation of the particle size, surface coverage, and the surface density of promoter particles is proposed.

Questions concerning the quantitative analysis of ultradisperse systems by XPS technique have been subject of inquiry in numerous works (see, e.g., [1-4]).The shell model or model of spherical shells is based on the assumptions that support particles are spherical in form[1,2]. The spherical shell model was expounded in detail by Frydman et al. in [2]. However, the expressions derived in [2] for the intensity of XPS lines (namely formulae (13), (17)) are correct only in the situation of $\lambda_{pp} = \lambda_{ps}$, $\lambda_{ss} = \lambda_{sp}$ (where λ_{pp} is the inelastic mean free path of photoelectrons from the studied element of the promoter during their passage through the promoter material, λ_{ps} is the inelastic mean free path of photoelectrons from the studied element of the promoter during their passage through the support material, λ_{ss} is the inelastic mean free path of photoelectrons from the studied element of the support during their passage through the support material, λ_{sp} is the inelastic mean free path of photoelectrons from the studied element of the support during their passage through the promoter material). In the cases where the inelastic mean free paths of photoelectrons in the material of a support (substrate) and in that of a promoter differ greatly, the application of formulae (13) and (17) derived in [2] can lead to essential errors.

Within the scope of our model, we suggest exact expressions for XPS intensities allowing for differences in inelastic mean free paths of photoelectrons in a support and in a supported phase (promoter) in the case of systems with a low specific surface area.

Henceforward, subscripts s and p will be used to denote a support and a promoter respectively.

According to this model, a sample is considered to be a layer of spherical particles of a support, on whose surface there is a promoter in the form of layers of thickness t_p (Fig. 1).

Henceforth, it is assumed that, in the course of deposition of a layer on the support surface, the specific surface area of the support, i.e. the sizes of its particles, will not change.

The mean radius of particles s can be expressed in terms of specific surface S_0 and density ρ_s of the support material in the following form:

$$R_s = \frac{3}{\rho_s S_0}. \tag{1}$$

The surface coverage f of support particles by a promoter is equal to the probability of finding a completely covered particle in a surface layer of the sample and is defined as

$$f = \frac{R_s^3 m_p \rho_s}{[(R_s + t_p)^3 - R_s^3](100 - m_p)\rho_p}, \tag{2}$$

where m_p – content of the promoter in the sample (in units of wt.%); ρ_p – density of the promoter material.

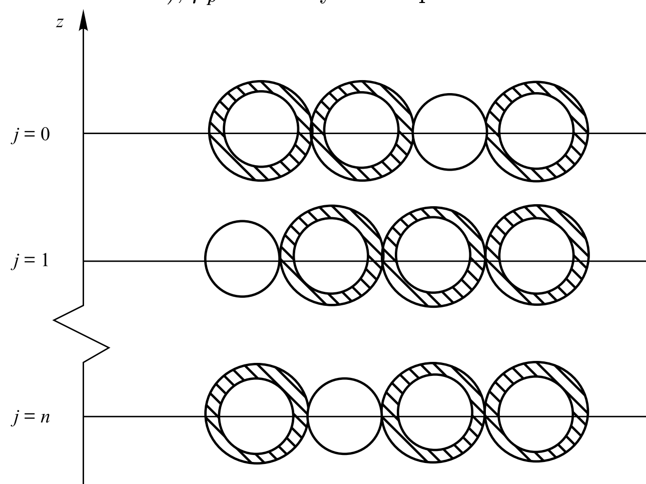

Fig. 1. Schematic representation of a sample within the scope of the shell model. Particles of a support are denoted by open circles; layers of a promoter are denoted by hatched shells

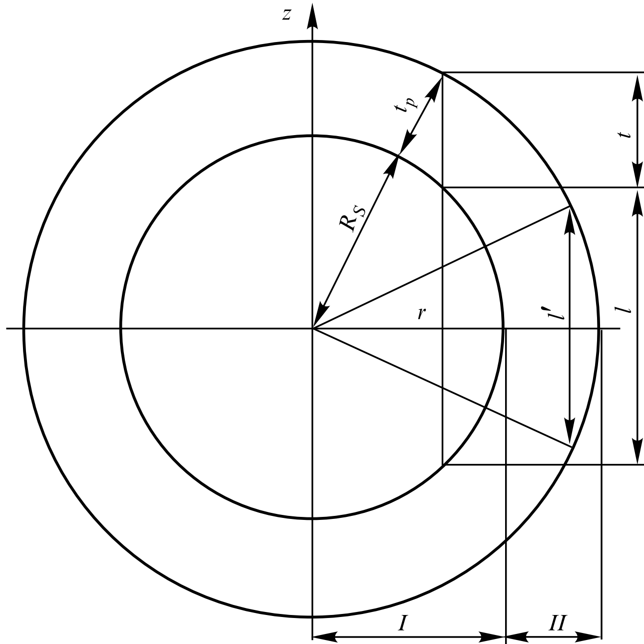

Fig. 2. Schematic representation of a spherical support particle of radius R_s covered by a promoter layer of thickness t_p. *I* and *II* are regions of integration

Now we calculate the number of photoelectrons from the support emitted in direction **z** into a solid angle $d\Omega$ for particles that are not covered by the promoter (N_{s1}) and for particles that are covered by the promoter (N_{s2}). The probability of finding particles that are not covered by the promoter is equal to $1-f$. Thus, the number of photoelectrons emitted in direction z as a result of ionization in volume dV at distance l from the surface of particle s is equal to

$$dN_{s1}=(1-f)I\frac{d\sigma_s}{d\Omega}d\Omega n_s\exp\left(-\frac{l}{\lambda_{ss}}\right)dVN_{\text{eff}}, \quad (3)$$

where I – intensity of X-radiation; n_s – concentration of the studied atoms in the support material; $\frac{d\sigma_s}{d\Omega}$– differential cross-section for ionization of the electronic level under consideration; N_{eff} – effective number of particles in the analyzed layer.

When the integration over the spherical particle volume is conveniently performed using the system of cylindrical coordinates ($dV = rdrd\varphi dz$, $l=\sqrt{R_s^2-r^2}-z$) and the distribution of atoms within the particle volume, n_s, is assumed independent of r, φ and z, we have

$$N_{s1}=\int_0^{2\pi}\int_0^{R_s}\int_{-\sqrt{R_s^2-r^2}}^{\sqrt{R_s^2+r^2}}(1-f)I\frac{d\sigma_s}{d\Omega}d\Omega n_s\times$$

$$\times\exp\left(-\frac{\sqrt{R_s^2-r^2}-z}{\lambda_{ss}}\right)N_{\text{eff}}rdzdrd\varphi=$$

$$=(1-f)I\frac{d\sigma_s}{d\Omega}d\Omega n_s 2\pi\lambda_{ss}N_{\text{eff}}\times$$

$$\times\int_0^{R_s}\left[1-\exp\left(-2\frac{\sqrt{R_s^2-r^2}}{\lambda_{ss}}\right)\right]rdr. \quad (4)$$

As a result of the integration, we get

$$N_{s1}=(1-f)I\frac{d\sigma_s}{d\Omega}d\Omega n_s 2\pi\lambda_{ss}\times$$

$$\times\frac{1}{2}R_s^2(1-\xi(R_s/\lambda_{ss}))N_{\text{eff}}, \quad (5)$$

where the function

$$\xi(R_s/\lambda_{ss})=\frac{1}{2}\left[\left(\frac{R_s}{\lambda_{ss}}\right)^2-\right.$$

$$\left.-\exp\left(-\frac{2R_s}{\lambda_{ss}}\right)\left(\frac{2R_s}{\lambda_{ss}}+\frac{R_s^2}{\lambda_{ss}}\right)\right]. \quad (6)$$

In the same way, it is possible to calculate the number of photoelectrons N_{s2} in the case of support particles covered by a promoter (Fig. 2). The probability of finding a particle of this type is equal to f. Thus,

$$N_{s2}=\int_0^{2\pi}\int_0^{R_s}\int_{-\sqrt{R_s^2-r^2}}^{\sqrt{R_s^2-r^2}}fI\frac{d\sigma_s}{d\Omega}d\Omega n_s\times$$

$$\times\exp\left(-\frac{\sqrt{R_s^2-r^2}-z}{\lambda_{ss}}\right)\exp\left(-\frac{t}{\lambda_{sp}}\right)\times$$

$$\times N_{\text{eff}}rdzdrd\varphi=fI\frac{d\sigma_s}{d\Omega}d\Omega n_s 2\pi\lambda_{ss}N_{\text{eff}}\times$$

$$\times\int_0^{R_s}\left[1-\exp\left(-\frac{2\sqrt{R_s^2-r^2}}{\lambda_{ss}}\right)\right]\exp\left(-\frac{t}{\lambda_{sp}}\right)rdr, \quad (7)$$

where

$$t=\sqrt{(R_s+t_p)^2-r^2}-\sqrt{R_s^2-r^2}. \quad (8)$$

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As a result, the number of photoelectrons $N_{s,j=0}$ from the first layer ($j = 0$) of the support particles will be equal to the sum of N_{s1} and N_{s2}, i.e.,

$$N_{s,j=0} = N_{s1} + N_{s2}. \tag{9}$$

We next derive expressions for a photoelectron flux from a promoter. In this case the required integration is conveniently performed over two regions *I* and *II* (see Fig.2). At $z > 0$, the number of photoelectrons for region *I* can be written as

$$N_{p1} = fI\frac{d\sigma_p}{d\Omega}d\Omega n_p 2\pi\lambda_{pp}N_{\text{eff}}\times$$

$$\times\int_0^{R_s}\left[1-\exp\left(-\frac{t}{\lambda_{pp}}\right)\right]rdr. \tag{10}$$

For region *I* at $z < 0$, the corresponding number is

$$N_{p2} = fI\frac{d\sigma_p}{d\Omega}d\Omega n_p 2\pi\lambda_{pp}N_{\text{eff}}\int_0^{R_s}\left[1-\exp\left(-\frac{t}{\lambda_{pp}}\right)\right]\times$$

$$\times\exp\left(-\frac{2\sqrt{R_s^2-r^2}}{\lambda_{ps}}\right)\exp\left(-\frac{t}{\lambda_{pp}}\right)rdr. \tag{11}$$

For region *II*, we have

$$N_{p3} = fI\frac{d\sigma_p}{d\Omega}d\Omega n_p 2\pi\lambda_{pp}N_{\text{eff}}\times$$

$$\times\int_{R_s}^{R_s+t_p}\left[1-\exp\left(-\frac{2\sqrt{(R_s+t_p)^2-r^2}}{\lambda_{pp}}\right)\right]rdr. \tag{12}$$

Then, the total flux of photoelectrons from the upper layer ($j = 0$) of a promoter can be defined as

$$N_{p,j=0} = N_{p1} + N_{p2} + N_{p3}. \tag{13}$$

As a result, the ratio of the numbers of photoelectrons, $N_{p,j=0}/N_{s,j=0}$ for the upper layer ($j = 0$) is equal to

$$\frac{N_{p,j=0}}{N_{s,j=0}} = \frac{fI\frac{d\sigma_p}{d\Omega}d\Omega n_p 2\pi\lambda_{pp}}{I\frac{d\sigma_s}{d\Omega}d\Omega n_s 2\pi\lambda_{ss}}\frac{F_1}{F_2}, \tag{14}$$

where

$$F_1 = \int_0^{R_s}\left[1-\exp\left(-\frac{t}{\lambda_{pp}}\right)\right]rdr + \int_0^{R_s}\left[1-\exp\left(-\frac{t}{\lambda_{pp}}\right)\right]\times$$

$$\times\exp\left(-\frac{2\sqrt{R_s^2-r^2}}{\lambda_{ps}}\right)\exp\left(-\frac{t}{\lambda_{pp}}\right)rdr + \int_{R_s}^{R_s+t_p}[1-$$

$$-\exp\left(-\frac{2\sqrt{(R_s+t_p)^2-r^2}}{\lambda_{pp}}\right)\Bigg]rdr, \tag{15}$$

and

$$F_2 = f\int_0^{R_s}\left[1-\exp\left(-\frac{2\sqrt{R_s^2-r^2}}{\lambda_{ss}}\right)\right]\times$$

$$\times\exp\left(-\frac{t}{\lambda_{sp}}\right)rdr + (1-f)\frac{1}{2}R_s^2[1-\xi(R_s/\lambda_{ss})]. \tag{16}$$

It is easy to show that the ratio n_p/n_s can be written as

$$\frac{n_p}{n_s} = \left(\frac{c_p}{c_s}\right)\frac{R_s^3}{f[(R_s+t_p)^3-R_s^3]}, \tag{17}$$

where c_s – atomic concentration of the studied element s in the sample; c_p – atomic concentration of the studied element of the promoter in the sample.

When allowing for Eq. (17), neglecting the differences in asymmetry parameters, and ignoring losses of the main peak at the expense of satellites, the ratio of the intensities of photoelectron lines for the upper layer ($j = 0$) can be written as

$$\frac{I_{p,j=0}}{I_{s,j=0}} = \frac{T_{E_k,p}}{T_{E_k,s}}\left(\frac{c_p}{c_s}\right)\frac{\sigma_p}{\sigma_s}\frac{\lambda_{pp}}{\lambda_{ss}}\times$$

$$\times\frac{R_s^3}{[(R_s+t_p)^3-R_s^3]}\frac{F_1}{F_2}, \tag{18}$$

where T_{E_k} – spectrometer transmission; E_k – kinetic energy of the studied electrons; σ_s – cross-section for photoionization involving the studied electronic level of support atoms; σ_p – cross-section for photoionization involving the studied electronic level of promoter atoms.

The expression derived can be applied for analyzing systems with a low specific surface area ($R_s \gg 5\lambda_{ss}$).

Thus, the numerical solution of this equation (using experimental data on the relative intensities of lines in photoelectron spectra) makes it possible to find the thickness of a promoter and calculate the surface coverage.

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МОДЕЛЬ ОБОЛОНОК ДЛЯ КІЛЬКІСНОГО АНАЛІЗУ НАНЕСЕНИХ КАТАЛІЗАТОРІВ МЕТОДОМ РФС: СИСТЕМИ З НИЗЬКОЮ ПИТОМОЮ ПОВЕРХНЕЮ

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Р е з ю м е

Розроблено модель оболонок для кількісного аналізу нанесених систем з низькою питомою поверхнею методом рентгенівської фотоелектронної спектроскопії. Запропоновано нову методику розрахунку розмірів поверхневих кластерів, ступеня заповнення поверхні та поверхневої щільності частинок нанесеної фази.

МОДЕЛЬ ОБОЛОЧЕК ДЛЯ КОЛИЧЕСТВЕННОГО АНАЛИЗА НАНЕСЕННЫХ КАТАЛИЗАТОРОВ МЕТОДОМ РФС: СИСТЕМЫ С НИЗКОЙ УДЕЛЬНОЙ ПОВЕРХНОСТЬЮ

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Р е з ю м е

Разработана модель оболочек для количественного анализа нанесенных систем с низкой удельной поверхностью методом рентгеновской фотоэлектронной спектроскопии. Предложена новая методика расчета размеров поверхностных кластеров, степени заполнения поверхности и поверхностной плотности частиц нанесенной фазы.