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

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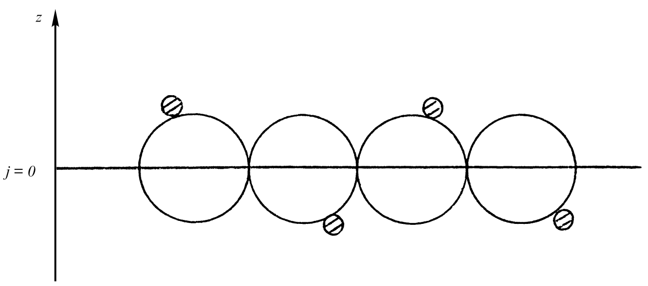
A sphere model for quantitative analysis of supported catalysts with a low specific surface area by X-ray photoelectron spectroscopy method is developed. New method for estimation of particle size, surface coverage and the surface density of promoter particles is proposed.

The representation of a support in the form of spherical particles and not in the form of infinite sheet [1,2] is one of the primary concepts of another approach to modelling disperse supported systems. In the majority of cases, this approach proved to be more adequate physically[3,4].The present work is devoted to the development of the sphere model in the case of supported systems with a low specific surface area.

According to the present model, the sample is considered to be in the form of a layer of spherical particles of a support (s), on whose surface there are uniformly distributed noninteracting particles of a promoter (p) (Figure). These particles are assumed to be noninteracting in the sense that effects related to their overlapping ("masking") one another may be ignored (in particular, one may ignore the absorption of electrons that have passed through a particle by neighbouring particles within the same layer). Henceforth, it is supposed that, during the course of deposition of promoter particles on the surface of a support, the specific surface area of the support and, consequently, size of its particles will not change.



Diagrammatic representation of a sample with a low specific surface in the form of a layer of particles within the scope of the sphere model. The support particles are designated by large open circles, and the promoter particles are designated by small hatched circles

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

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

Each promoter particle "casts a shadow" on the support surface, with every shadowed portion taken to be equal to πR_p^2. Thus, the degree of covering the support surface by promoter particles, f, can be expressed in terms of the content of the promoter substance in the sample, m_p (in units of wt.%), in the following form:

$$f = \frac{m_p R_s \rho_s}{(100 - m_p) 4 R_p \rho_p}. \tag{2}$$

Let ρ_{surp} denote the averaged surface density of promoter particles on the support. In this case, f can be also written as

$$f = \rho_{\mathrm{surp}} \pi R_p^2. \tag{3}$$

When calculating the number of electrons emitted by the support atoms in direction z, it is expedient to take account of the fact that the corresponding values of f are small for the majority of real systems, and, as was shown in [1], the absorption of photoelectrons during their passage through a surface layer of promoter particles may be ignored. The number of photoelectrons emitted in direction z into a solid angle $d\Omega$ as a result of ionization in volume dV at distance l from the surface of a support particle is equal to

$$dN_s = I \frac{d\sigma_s}{d\Omega} d\Omega n_s \exp\left(-\frac{l}{\lambda_{ss}}\right) N_{\mathrm{eff}} dV, \tag{4}$$

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 an electronic level of a support atom; λ_{ss} – inelastic mean free path of electrons from the support atom during their passage through the support material; N_{eff} – effective number of support particles in the analyzed layer (when the sample surface and mean radius of particles are approximately equal to 1 cm^2 and 10 nm, respectively, amounts to ca 10^{12} particles).

Integration of Eq. (4) over the spherical particle volume is advisable to perform in the system of cylindrical coordinates $dV = rdrd\varphi dz$ and $l = \sqrt{R_s^2 - r^2} - z$. Besides, it is assumed that the distribution of atoms within the particle volume does not depend on r, φ, and z. With these assumptions, we can write

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

$$\times \exp\left(-\frac{\sqrt{R_s^2-r^2}-z}{\lambda_{ss}}\right) N_{\text{eff}} rdzdrd\varphi. \quad (5)$$

The integration yields

$$N_s = I\frac{d\sigma_s}{d\Omega}d\Omega\pi R_s^2\lambda_{ss}\left[1-\xi(R_s/\lambda_{ss})\right]N_{\text{eff}}, \quad (6)$$

where the function

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

$$-\exp\Big(-\frac{2R_s}{\lambda_{ss}}\Big)\Big(\frac{2R_s}{\lambda_{ss}} + \frac{R_s^2}{\lambda_{ss}}\Big)\Big]. \quad (7)$$

The number of photoelectrons that are emitted in direction $\vec{z}$ from the promoter particles situated on the external side of the support ($z > 0$) can be written as

$$N_p(z>0) = I\frac{d\sigma_p}{d\Omega}d\Omega n_p \times$$

$$\times \iint \rho_{\text{surp}}\pi R_p^2\left[1-\xi(R_p/\lambda_{pp})\right]N_{\text{eff}}ds, \quad (8)$$

where the integration is performed with respect to the surface of the upper hemisphere. As a result, we get

$$N_p(z>0) = I\frac{d\sigma_p}{d\Omega}d\Omega n_p\rho_{\text{surp}}\pi R_p^2\left[1-\xi(R_p/\lambda_{pp})\right]\times$$

$$\times \int_0^{2\pi}\int_0^{R_s}\frac{R_s}{\sqrt{R_s^2-r^2}}rdrd\varphi N_{\text{eff}} \quad (9)$$

or

$$N_p(z>0) = I\frac{d\sigma_p}{d\Omega}d\Omega n_p f 2\pi R_s^2\lambda_{pp}\times$$

$$\times\left[1-\xi(R_p/\lambda_{pp})\right]N_{\text{eff}}, \quad (10)$$

where λ_{pp} is the inelastic mean free path of the promoter electrons passing through the promoter material.

When passing through the support, electrons from the promoter are subject to absorption in the layer of length $2\sqrt{R_s^2-r^2}$. With allowance for this fact, a similar expression for the number of photoelectrons from the promoter particles situated on the shadowed side of the support can be written as

$$N_p(z<0) = I\frac{d\sigma_p}{d\Omega}d\Omega n_p\rho_{\text{surp}}\pi R_p^2\left[1-\xi(R_p/\lambda_{pp})\right]\times$$

$$\times\int_0^{2\pi}\int_0^{R_s}\frac{R_s}{\sqrt{R_s^2-r^2}}\exp\left(-\frac{2\sqrt{R_s^2-r^2}}{\lambda_{ps}}\right)rdrd\varphi N_{\text{eff}}, \quad (11)$$

where λ_{ps} is the inelastic mean free path of electrons from the promoter passing through the support material. Essentially, in this case, we go from a layer of discrete promoter particles to a uniform radiative promoter sheath, whose properties are determined by surface coverage f and particle size R_p. As a result of the integration, we get

$$N_p(z<0) = N_p(z>0)\frac{\lambda_{ps}}{2R_s}\left[1-\exp\left(-\frac{2R_s}{\lambda_{ps}}\right)\right]. \quad (12)$$

Then, the ratio of the relevant numbers of photoelectrons for an upper layer ($j = 0$) is

$$\frac{N_p}{N_s} = \frac{\frac{d\sigma_p}{d\Omega}n_p f 2\lambda_{pp}[1-\xi(R_p/\lambda_{pp})]}{\frac{d\sigma_s}{d\Omega}n_s\lambda_{ss}}\times$$

$$\times\frac{\left(1+\frac{\lambda_{ps}}{2R_s}\left[1-\exp\left(-\frac{2R_s}{\lambda_{ps}}\right)\right]\right)}{[1-\xi(R_s/\lambda_{ss})]}. \quad (13)$$

Evaluation of the contribution to the total number of photoelectrons made by the promoter particles situated on the shadowed side of the support shows that, at $R_p > \lambda_{ps}$ the ratio $N_p(z>0)/N_p(z<0)$ is approximately equal to $\lambda_{ps}/2R_s$. At $R_s \approx 100$ Å and $\lambda_{ps} \approx 20$ Å, this ratio amounts to ca 10. Therefore, in the first approximation, the contribution made by the photoelectrons from the promoter particles situated on the shadowed side of the support may be ignored. At $R_s < \lambda_{ps}$, it is absolutely necessary to allow for particle layers to be situated at more large depths as well.

Now, let us consider the situation where $R_s \gg \lambda_{ps}$, which is the case for systems with a low specific surface area. Here, the ratio of the number of photoelectrons from the promoter to that from the support is

$$\frac{N_p}{N_s} = \frac{I\frac{d\sigma_p}{d\Omega} n_p f 2\pi R_s^2 \lambda_{pp} \left[1 - \xi(R_p/\lambda_{pp})\right]}{I\frac{d\sigma_s}{d\Omega} n_s \pi R_s^2 \lambda_{ss} \left[1 - \xi(R_s/\lambda_{ss})\right]}. \quad (14)$$

After reduction, we get

$$\frac{N_p}{N_s} = \frac{\frac{d\sigma_p}{d\Omega} n_p f 2\lambda_{pp} \left[1 - \xi(R_p/\lambda_{pp})\right]}{\frac{d\sigma_s}{d\Omega} n_s \lambda_{ss} \left[1 - \xi(R_s/\lambda_{ss})\right]}. \quad (15)$$

Thus, the intensity ratio for the relevant photoelectron lines can be written as

$$\frac{I_p}{I_s} = \frac{T_{E_{k,p}} \sigma_p n_p f 2\lambda_{pp} \left[1 - \xi(R_p/\lambda_{pp})\right]}{T_{E_{k,s}} \sigma_s n_s \lambda_{ss} \left[1 - \xi(R_s/\lambda_{ss})\right]}, \quad (16)$$

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 the support atoms; σ_p – cross-section for photoionization involving the studied electronic level of the promoter atoms.

It is easy to show that

$$\frac{n_p}{n_s} = \frac{c_p}{c_s} \frac{\rho_p(100 - m_p)}{\rho_s m_p}, \quad (17)$$

where c_p and c_s are atomic concentrations of the studied elements in the sample. Substituting the right sides of Eqs. (2) and (17) for f and n_p/n_s, respectively, in Eq. (16), we get

$$\frac{I_p}{I_s} = \frac{T_{E_{k,p}}}{T_{E_{k,s}}} \frac{c_p}{c_s} \frac{\sigma_p R_s \lambda_{pp} \left[1 - \xi(R_p/\lambda_{pp})\right]}{\sigma_s 2R_p \lambda_{ss} \left[1 - \xi(R_s/\lambda_{ss})\right]}. \quad (18)$$

It is evident from this ratio that, in the case of invariability of sizes (dispersity) of the promoter particles, there is a linear dependence of I_p/I_s on relative concentration c_p/c_s.

If the promoter layer on the support surface is monoatomic or monomolecular, the ratio R_s/λ_{pp} is small, so that

$$\frac{1 - \xi(R_p/\lambda_{pp})}{(R_p/\lambda_{pp})} = \frac{4}{3}. \quad (19)$$

Thus,

$$\left(\frac{I_p}{I_s}\right)_{\text{mono}} = \frac{T_{E_{k,p}}}{T_{E_{k,s}}} \left(\frac{c_p}{c_s}\right) \frac{\sigma_p 2R_s}{\sigma_s 3\lambda_{ss}[1 - \xi(R_s/\lambda_{ss})]}. \quad (20)$$

Tabulated values of the function $F(R_p/\lambda_{pp})$

R_p/λ_{pp}	F	R_p/λ_{pp}	F
0.0	1.3323	5.0	0.1960
0.1	1.2385	6.0	0.1644
0.2	1.1530	7.0	0.1414
0.3	1.0759	8.0	0.1240
0.4	1.0062	9.0	0.1104
0.5	0.9430	10.0	0.0995
0.6	0.8857	20.0	0.0499
0.7	0.8336	30.0	0.0333
0.8	0.7861	40.0	0.0250
0.9	0.7427	50.0	0.0200
1.0	0.7030	60.0	0.0167
2.0	0.4432	70.0	0.0143
3.0	0.3151	80.0	0.0125
4.0	0.2422	90.0	0.0111
5.0	0.1960	100.0	0.0100

It is trivially found from Eqs. (18) and (20) that

$$\left(\frac{I_p}{I_s}\right) \Big/ \left(\frac{I_p}{I_s}\right)_{\text{mono}} = \frac{3\left[1 - \xi(R_p/\lambda_{pp})\right]}{4(R_p/\lambda_{pp})}. \quad (21)$$

For convenience, let us introduce the function

$$F(R_p/\lambda_{pp}) = \frac{1 - \xi(R_p/\lambda_{pp})}{(R_p/\lambda_{pp})} \quad (22)$$

and tabulate its values (see Table).

Hence, it appears that, having found a numerical solution of Eq. (21) for R_p/λ_{pp} (here a use may be made of Table) and using formulae (1) and (20), one can estimate sizes R_p of promoter clusters. Once R_p is known, it is also possible from formulae (2) and (3) to estimate the degree of covering the surface by promoter particles as the well as the surface density of these particles.

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

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Р е з ю м е

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

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

И.В.Плюто, А.П.Шпак

Р е з ю м е

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