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Weaknesses of the pseudo-Voigt distribution used in the characterization of nanostructured materials based on the powder X-ray diffraction method

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The diffraction line broadening in X-ray powder pattern is analyzed by using the pseudo-Voigt distribution as well as the Generalized Fermi Function facilities. X-ray line broadening investigations of supported gold catalysts have been limited to finding the average crystallite size from the integral width or the full width at half maximum of the diffraction line. In the case of supported gold catalysts, it is generally difficult to perform satisfactory intensity measurements of the higher order (hkl) reflections. Therefore, the classical method of Warren and Averbach cannot be applied. In this paper we develop an analytical relation based on the pseudo-Voigt distribution that gives the Fourier transform of the true sample function. From the comparison analysis of the Fourier transform of the true sample function and its general relation we point out the weakness of the Voigt distribution used in the case of Au/SiO$_2$ catalyst. The same problem occurs on other nanostructured materials investigated by powder X-ray diffraction method. A reliable solution for this problem is to use the generalized Fermi function instead of Voigt distribution.

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1. Introduction

X-ray diffraction line profile analysis is a versatile nondestructive method that can be used in obtaining nanostructural information of the supported gold catalysts used in oxidation redaction, isotopic exchange and hydrogenation reactions. From the position and broadening of X-ray line profile (XRLP) one can obtain the imperfect crystallite structure in terms of the effective crystallite size and the microstrain as lattice disorder [1-3].

The purpose of this paper is to point out theoretical aspects that prove the weakness of the pseudo-Voigt distribution as X-ray line profile approximation further used in analyzing the metal nanoparticle size and the lattice distortion based on analytical relations developed by Warren and Averbach theory. The analytical and numerical results are exemplified by analyzing a sample of supported gold catalyst. The analytical models are implemented in our XRSIZE computer package program. The supported gold catalyst was prepared by homogeneous deposition-precipitation with urea on SiO$_2$ support. The precursor was HAuCl$_4$·3H$_2$O, Adrich, 99.999% purity. The theoretical gold content for the catalysts was 5% wt. The catalyst was calcined at 300 ^{o}C before the measurements [4]. The X-ray (111), (200), (220) and (311) diffraction data of supported gold catalyst were collected using Dron 2M setup, in Bragg-Brentano geometry with Ni filtered Cu K$_\alpha$ radiation, λ=1.5406 Å at room temperature. A NaI (Tl) detector was used; the signals were amplified and fed to a single channel analyzer read out by a personal computer [5].

2. Theoretical background

The X-ray diffraction pattern of a crystal can be described in terms of scattering intensity as function of scattering direction defined by the scattering angle 2θ, or by the scattering parameter $s=2\sin\theta/\lambda$, where λ is the wavelength of the incident radiation. Experimentally one can measure the integrated intensity profile function $h(2\theta)$ or $h(s)$ for the crystals. The experimental X-ray line profile (XRLP), *h*, represents the convolution between the true sample *f* and the instrumental function produced by a well-annealed sample, g, and it is described by the Fredholm integral Equation of the first kind [1],

$$h(s)=\int g(s^{*}-s)f(s^{*})\,ds^{*} \qquad (1)$$

From mathematical point of view, the true sample function, *f(s),* is a solution of Eq. (1) and can be obtained by Fourier transform method. If someone chooses this method, the true sample function can be obtained by the relationship,

$$H(L)=G(L)F(L), \qquad (2)$$

where *F(L)*, *H(L)* and *G(L)* are Fourier transforms (FT) of the true sample, experimental XRLP and instrumental function. The variable *L* is the perpendicular distance to the *(hkl)* reflection planes. The normalized *F(L)* can be described as the product of two factors, $F^{(s)}(L)$ and $F^{(\varepsilon)}(L)$. The factor $F^{(s)}(L)$ describes the contribution of crystallite size and stocking fault probability while the factor $F^{(\varepsilon)}(L)$ gives information about the microstrain of the lattice. Based on Warren and Averbach theory [1-3], the general form of the Fourier transform of the true sample for cubic lattices is given by the relationships,

$$F^{(s)}(L)=e^{-\frac{|L|}{D_{eff}(hkl)}},$$

$$F^{(\varepsilon)}(L)=e^{-\frac{2\pi^2\left\langle\varepsilon_L^2\right\rangle_{hkl}h_0^2L^2}{a^2}}, \qquad (3)$$

where $D_{eff}(hkl)$ is the effective crystallite size, $<\varepsilon^2>_{hkl}$ is the microstrain of the lattice, $h_0^2=h^2+k^2+l^2$.

The general form of the true sample function *f(s)* is obtained by inverse Fourier transform of *F(L)*

$$f(s)=\int_{-\infty}^{\infty}e^{-\beta L^2-\gamma|L|}e^{2\pi isL}dL=$$

$$=\sqrt{\frac{\pi}{\beta}}\exp\left[\frac{\gamma^2-(2\pi s)^2}{4\beta}\right]\left\{\mathrm{Re}\left[erfc\left(\frac{\gamma-2\pi is}{2\sqrt{\beta}}\right)\right]\cos\frac{\pi\gamma s}{\beta}-\mathrm{Im}\left[erfc\left(\frac{\gamma+2\pi is}{2\sqrt{\beta}}\right)\right]\sin\frac{\pi\gamma s}{\beta}\right\}, \qquad (4)$$

where $\beta=\dfrac{2\pi^2\left\langle\varepsilon_L^2\right\rangle h_0^2}{a^2}$, $\gamma=\dfrac{1}{D_{eff}}$, $s=2\left(\dfrac{\sin\theta}{\lambda}-\dfrac{\sin\theta_0}{\lambda}\right)$

and *erfc* is the complementary error function[6]. The Fourier transform magnitude of the true sample can be obtained by solving the Eq. (1). Many authors have solved this equation by adopting a large variety of the XRLP approximations [7-10].

3. Results and discussion

Practically, it is not easy to obtain accurate values of the crystallite size and microstrain without extreme care in the experimental measurements and analysis of XRD data. The Fourier analysis of XRLP validity depends strongly on the magnitude and the nature of the errors propagated in the data analysis. In paper [11] are treated three systematic errors: uncorrected constant background, truncation and the effect of the sampling for the observed profile at a finite number of points that appear in discrete Fourier analysis. In order to minimize the propagation of these systematic errors, a global approximation of the XRLP is adopted instead of the discrete calculus. The experimental XRLP (111), (200), (220) and (311) of the Au/SiO$_2$ and the instrumental spectrum of the SiO$_2$ powder as standard correction are shown in Figs. 1 and 2.

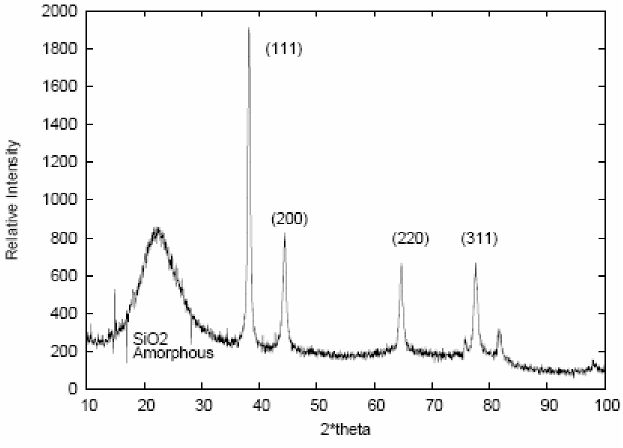

Fig. 1. The relative intensity of (111), (200), (220) and (311) XRLP forAu/SiO$_2$ sample.

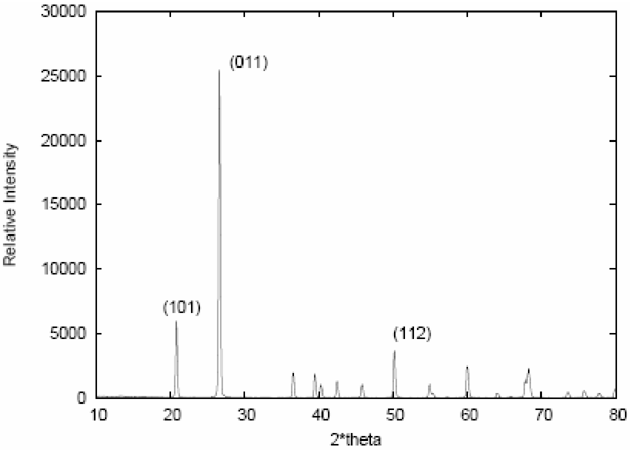

Fig. 2. The relative intensity of (101), (011) and (112) XRPL for SiO$_2$ powder very well crystallized as the instrumental function.

Further, we carried out corrections for the background and for the $K_{\alpha2}$ doublet, the second one by Rachinger approximation [12]. The analysis of the diffraction line broadening in X-ray powder pattern was analytically calculated using the pseudo-Voigt, (pV), as well as the Generalized Fermi Function (GFF) facilities [2,7]. The pseudo-Voigt distribution has the following form,

$$pV(s^*)=b_2\left\{\frac{b_1}{1+\left(\frac{s^*}{b_4}\right)^2}+(1-b_1)\exp\left[-\frac{1}{2}\left(\frac{s^*}{b_4}\right)^2\right]\right\} \qquad (5)$$

where $\mathrm{s}=2\dfrac{\sin\theta}{\lambda}$, $s_0=2\dfrac{\sin\theta_0}{\lambda}=\left|\dfrac{1}{d_{hkl}}\right|=b_3$ and $s^*=s-s_0$. The parameters b$_1$, b$_2$, b$_3$ and b$_4$ supply information related to the mixing ratio of Lorentian and Gaussian contribution, the magnitude, the gravity center and the broadening of the XRLP. If we use Eq. (5) for approximating the experimental sample *h(s)* as well as for the instrumental function *g(s),* we will obtain for the Fourier transform of the true sample function the following relation,

$$F(L)=\frac{\sqrt{2\pi}\,b_{2h}\,b_{4h}(1-b_{1h})\exp\left(-\beta_h L^2\right)+\pi b_{1h}\,b_{2h}\,b_{4h}\exp\left(-\gamma_h|L|\right)}{\sqrt{2\pi}\,b_{2g}\,b_{4g}(1-b_{1g})\exp\left(-\beta_g L^2\right)+\pi b_{1g}\,b_{2g}\,b_{4g}\exp\left(-\gamma_g|L|\right)} \qquad (6)$$

where $\beta_h = 2\pi^2 b_{4h}^2, \gamma_h = 2\pi b_{4h}$, $\beta_g = 2\pi^2 b_{4g}^2$ and $\gamma_g = 2\pi b_{4g}$. The subscripts *g* and *h* refer to the instrumental and the experimental XRLP. Because the parameters β and γ from Eqs. (3-4) are positive numbers, the new function F(L) has to be monotonically increasing for negative values of L variable and monotonically decreasing for the positive axis. Based on this reason any analytical distribution that approximates both the experimental XRLP and the instrumental function, must have the Fourier Transform of the true sample with the same mathematical properties as the physical model given by Eq. (3) for obtaining accurate values of nanostructural parameters of the investigated samples.

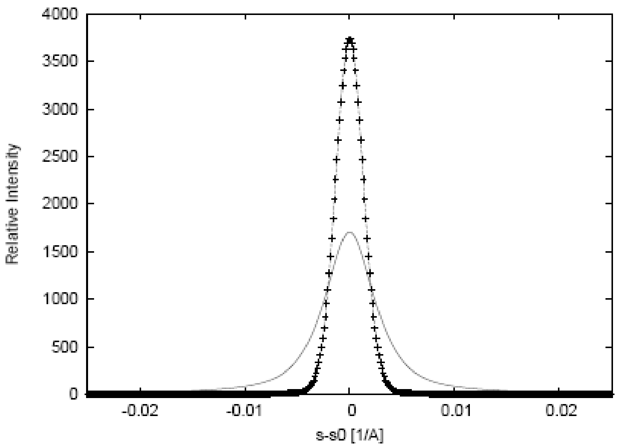

Fig. 3. The (111) of Au/SiO2 and (011) XRLP of the instrumental function approximated by pseudo-Voigt distributions, h function (solid line), g function (−+−).

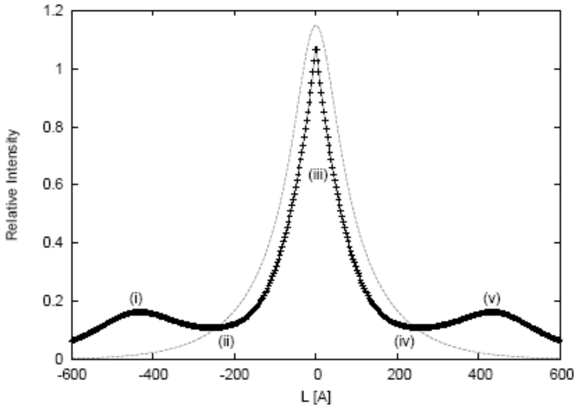

Fig. 4. The Fourier transforms of the true sample determined by the pseudo - Voigt distribution (−+−) and the GFF approximation (−−−).

By Lavenberg-Marquard fit of Eq.(5) we evaluated the best parameters for *h(s)* and *g(s)* XRLP. The values of each parameters for (111) experimental XRLP and (011) instrumental function are: b_{1h}=0.748246, b_{2h}=0.170934×10^4, b_{4h}=0.002688, b_{1g}=0.063081, b_{2g}=0.373898×10^4 and b_{4g}=0.001326. Fig. 3 present the Fourier transforms *H(L)* and *G(L)* of the (111) for Au/SiO$_2$ and (011) for SiO$_2$ XRLP. By using Eq. (6) we determined the Fourier transform of the true sample drawn in Fig. 4. By analyzing the *F(L)* function in the interval -600 and 600 Å from Fig. 4 we can find five extreme values, from which only the third one has physical signification. At least for this sample the pseudo-Voigt distribution used for *h* and g XRLP approximation do not supply reliable information about the nanostructure parameters of the investigated sample. In the same figure we have drawn the Fourier transform of the true sample using the analytical model based on the GFF distribution [2,7]. The GFF model is in good accordance, from mathematical point of view, with general relation given by Eq. (3). The strong points of the GFF model are the simplicity and the mathematical elegance of the analytical magnitude, Fourier transform and the integral width of the true XRLP [2-3]. The robustness of the GFF approximation for the XRLP arises from the possibility of using the analytical form of the Fourier transform instead of a numerical fast Fourier transform (FFT). It is well known that the validity of the numerical FFT depends on the filtering technique adopted [13-14]. Therefore the validity of the microstructural parameters are closely related to the accuracy of the Fourier transform magnitude of the true XRLP [2-3,7]. In the papers [2-3], based on a compared analysis of the residual indexes, we have shown that the GFF approximation has a low precision in approaching the instrumental function but it has a good precision in fitting the experimental XRLP. The pseudo-Voigt distribution has an acceptable residual index value for narrow and large profiles, but it is less acceptable for profiles having medium integral widths.

4 Conclusions

In order to obtain reliable information such as the effective crystallite size and microstrain of the lattice by powder X-ray diffraction for nanostructured materials it is very important to choose an adequate distribution for the global approximation of the XRLP as well as for the instrumental correction. Some times the classical pseudo-Voigt distribution used in data analysis can supply unacceptable nanostructured results. As an alternative the GFF distribution can offer valuable results.

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