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SAXS study of coated porous silicas

A. BENEDETTI, S. CICCARIELLO*, F. PINNA** and G. STRUKUL**

Dipartimento di Chimica-Fisica, Calle S. Marta DD2137, 30123 Venezia, Italy

** Dipartimento di Fisica 'G. Galilei' and sez. INFN, via Marzolo 8, 35131 Padova, Italy*

*** Dipartimento di Chimica Industriale, Calle S. Marta DD2137, 30123 Venezia, Italy*

Abstract - The small-angle x-ray intensities scattered (SAXS) by four reversed phase silica (RPS) samples are analyzed. The RPS's have been obtained by coating two different porous silica supports with dimethyloctyl- and with dimethyloctadecyl-(chloro)silane. From the observed intensities it is possible to estimate the mean electron-densities of the films as well as the mean silica-surface per coating molecule.

1 - Introduction and theoretical model

It has been recently pointed out that SAXS can be useful for characterizing coatings in porous materials as, e.g., reversed phase silicas. The observed intensities in fact, turn out to be sensitive to the loadings of the samples as well as to the length of the coating molecules[1]. Structural information on the coating films can be obtained by modelling the samples as consisting of three homogeneous phases, the bulk silica, the void regions (pores) and the film of the coating molecules, each characterized by a *constant* electron density: $n_1, n_2 (= 0)$ or n_3 , respectively, the thickness (δ) of the film region being *constant*[2]. From this model, it follows that the silica-film and the film-void interfaces are parallel. Thus the SAXS intensity, at large h 's, is found to be equal to[3]

$$I_{lat}(h) = \frac{2\pi S \alpha(\nu) n_{12}^2}{h^4} [1 + \mathcal{R}(\nu) \cos(h\delta)] \quad (1)$$

or to

$$J_{lat}(h) = \frac{\pi^2 S \alpha(\nu) n_{12}^2}{h^3} [1 + \mathcal{R}(\nu) \varphi_0(h\delta)], \quad (2)$$

depending on the collimation geometry. Here, S denotes the area of silica surface, while $\varphi_0(x)$ is a function defined elsewhere[4] and characterized by a damped oscillatory behaviour. The remaining quantities are defined as follows:

$$n_{ij} \equiv n_i - n_j, \quad i, j = 1, 2, 3, \quad \nu \equiv (n_{13} - n_{32})/n_{12} \quad (3a, b),$$

$$\alpha(\nu) \equiv (1 + \nu^2)/2 \quad \text{and} \quad \mathcal{R}(\nu) \equiv (1 - \nu^2)/(1 + \nu^2). \quad (3c, d)$$

According to eq.s (1) and (2), a Porod plot of the intensities should show an oscillatory deviation, whose frequency decreases as the length of the coating molecules increases, while its amplitude increases as the sample loading is increased (see eq.s (3b) and (3d)). Figure 1 of this paper as well as figures 1 and 2 of [2] show such a behaviour.

Figure 1. Porod plots of the intensities. Symbols refer to experimental values, while curves represent fitted curves. From the bottom, each curve has been vertically shifted by 0, 0.2, 0.7 and 0.9 units, respectively.

Therefore the parameters δ , $\mathcal{R}$, $(\alpha n_{12}^2 S)$ and β_{ck} (this added parameter represents the constant "Laue background" due to electron density fluctuations on atomic scale[5]) can be estimated by minimizing the quantity

$$\chi_{slit}^2 = \sum_{h_I \leq h_j \leq h_F} \left\{ \left[(J_{exp}(h_j) - \beta_{ck}) - J_{lat}(h_j) \right] / J_{w,j} \right\}^2. \quad (4)$$

$J_{exp}(h_j)$ denotes the 'ideal slit' experimental intensity at the j th momentum transfer value h_j , $J_{lat}(h_j)$ is given by eq. (2) and $J_{w,j} \propto [J_{exp}(h_j)]^\varpi$, with $\varpi = 1/2$ or 1 depending on whether the intensities are measured at fixed time or at fixed counts[6]. h_I and h_F denote the lower and upper bounds of the asymptotic region. The considered h_F values correspond to the largest observed scattering angles, while the h_I 's are roughly equal to the positions of the (1st) peak in the Porod plots.

2 - Numerical analysis and results

The aim of this paper is to better assess the accuracy of the technique by comparing the resulting parameters with the values obtained by chemical analysis. The Table reports the results obtained by best-fitting the intensities relevant to some coated silica samples. The intensities were collected with a Kratky camera equipped with an electronic step scanner[2]. Samples ME-RP8 and ME-RP18 belong to Merck's Lichroprep series obtained by fully derivatizing a silica support, having pores of 100Å, with dimethyloctyl- and with dimethyloctadecyl-chlorosilane, respectively. Samples VE-RP8 and VE-RP18 have been similarly prepared in our laboratory starting from the AKZO Chemie F-22 silica support with pores of 90Å. Therefore, the two sets of fully loaded samples differ only in the geometry of the supports.

Beside the quantities already defined, the remaining quantities in the Table are defined as follows: $\tau \equiv n_3/n_1$, s is the support surface area per coating molecule, $\bar{\sigma} \equiv (S/(V\Phi(\nu, \{\phi\})))$ where

$$\Phi(\nu, \{\phi\}) \equiv [\phi_1\phi_2 + (1+\nu)^2\phi_1\phi_3/4 + (1-\nu)^2\phi_2\phi_3/4]. \quad (5)$$

Finally, S_{ru} and Q_{Pru} denote the film area and the Porod invariant values obtained from the intensity profiles in relative units.

Table

δ : film thickness; $\mathcal{R}(\nu)$: defined by eq. (3c); $\tau \equiv n_3/n_1$; $\bar{\sigma}$: defined above eq. (5); s : silica surface area per coating molecule; β_{ck} : theoretical background; $n_{12}^2 S_{ru} = (n_1 - n_2)^2 S_{ru}$: proportional to the support surface; Q_{Pru} : Porod invariant obtained from the relative unit intensity; $h_I - h_F$: extrema of the best-fit h -range; $\bar{\chi} \equiv \chi^2/(N_{exp} - N_{par})$: statistical indicator of the fit goodness.

sample	$\delta[\text{\AA}]$	$\mathcal{R}(\nu)$	τ	$\bar{\sigma}[\text{\AA}^{-1}]$	$s[\text{\AA}^2]$
ME-RP 8	13±4	0.43	0.82±0.06	0.19	13±5
ME-RP18	15±2	0.76	0.68±0.05	0.15	25±4
VE-RP 8	11±6	0.19	0.91±0.15	0.18	14±6
VE-RP18	14±3	0.34	0.85±0.07	0.18	22±5
sample	β_{ck}	$n_{12}^2 S_{ru}$	Q_{Pru}	$h_I - h_F[\text{\AA}^{-1}]$	$\bar{\chi}$
ME-RP 8	14±6	0.19±0.02	318	0.06-0.35	0.78
ME-RP18	16±9	0.15±0.02	239	0.06-0.35	1.87
VE-RP 8	31±7	0.18±0.04	310	0.08-0.35	0.03
VE-RP18	24±6	0.17±0.02	271	0.08-0.35	0.07

Inspection of the results allows one to estimate the consistency and accuracy which can be obtained by the aforesaid analysis. Since the analyzed samples have approximately the same volume and have been similarly prepared, $n_{12} S_{ru}$, β_{ck} and $\bar{\sigma}$ should depend mainly on the support. On the contrary, δ , s and, to a lesser extent, τ should depend

mainly on the length of the coating molecules. These properties appear to be reasonably verified.

3 - Further checks and conclusion

Further checks are possible due to the noted uniformity in sample preparation and to the use of the same experimental apparatus. In this case: $Q_{Pru,l} = Cn_{12}^2\Phi(\nu_l, \{\phi_l\})$, where the index l labels the different RPS's obtained from the same support. (Note that the constant C is independent of l .) It is reasonable to assume that the derivatization of a silica support amounts to leaving ϕ_1 constant and to decreasing ϕ_2 by the film volume fraction $\phi_{3,l} \approx S\delta_l/V$. Therefore, when the mass and $Q_{Pru,0}$ relevant to the silica support sample are known, taking the ratios of the $Q_{Pru,l}$'s with $Q_{Pru,0}$ and using the ν_l values resulting from the $\mathcal{R}(\nu)$'s reported in the table, both S/V and ϕ_1 can be determined. For the AKZO F-22 support $Q_{Pru,0} = 314$ and it results that the specific surface and the void-volume fraction are equal to $600\text{m}^2/\text{g}$ and 0.66 respectively, while the manufacturer nominal values are $400\text{m}^2/\text{g}$ and 0.80 .

A further check on the s -values can be obtained by measuring the RPSs' carbon content by elemental analysis. The weight percents of carbon were found equal to 8.46% and to 10.98% in samples VE-RP8 and VE-RP18, respectively. This corresponds to one coating molecule per 17 and per 29 SiO_2 molecules, respectively. The support being the same and its void-volume fraction high, the ratio $17/29$ must be approximately equal to the ratio of the corresponding s -values reported in the table, i.e. $14/22$. For the ME-RP8 and ME-RP18 samples, the carbon weight percents are: 9.64 and 17.24 , which imply a coating molecule per 18 SiO_2 molecules in both samples. Thus, the ratio of the corresponding s 's should be one, while the table results give $13/25$.

In conclusion, by eq.s (1-3) the analysis of the deviations from the Porod behaviour of the small-angle intensities, scattered by coated porous materials, provides reliable structural information (thickness, electron density, area per coating molecule) on the coating films.

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* Author for correspondence.

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