Influence of treatment with sulfuric acid on the angularity of a zirconia system

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Small-angle X-ray scattering (SAXS) measurements have been used to determine the influence of sulfation on the morphology of zirconia particles. Two samples were investigated: a zirconium oxide powder before (sample A) and after (sample B) a sulfation treatment with H_2SO_4. The decrease of about one order of magnitude in the angularity value for sample **B** provided quantitative proof of transmission electronic microscopy (TEM) evidence.

Interest in the use of zirconia both as a catalyst and as a support has been growing in recent years. In particular, the superacid properties shown by zirconia sulfates have prompted new studies which seek to understand how sulfate promotion generates superacidity and how, in general, the sulfate interacts with zirconium oxide, modifying the initial structure and microstructure of the sample.[1]

Recently, some TEM micrographs have shown that the sulfation, by H_2SO_4, of a pre-calcined Zr hydride powder affects the contours of crystalline particles, which become more rounded.[2] Apart from general considerations on the possible cause of this phenomenon, no further comments on the shape of the particles were added. Obviously, the analysis of some electron micrographs provides only a qualitative estimate of the particle shapes.

The aim of this short paper is to demonstrate that SAXS experiments give a quantitative determination of the smoothness of the particles through the measurement of the so-called angularity. It should be recalled that this quantity, first introduced by Porod[3] and Mering and Tchoubar,[4] is equal to zero when the interphase surface is smooth, *i.e.* when it has no edges and no contact points. When the surface is not smooth, the angularity is positive. It increases as the length of the edges increases and as the related dihedral angles approach zero.[5,6] The angularity can be determined fairly easily and unambiguously from the scattered intensity by using some convenient parametrizations of the correlation function both for two and for N component system.[7,8] However, although quantitative analysis is quite straightforward, it has never been used to compare the effect on the particle surface when the same sample has undergone suitable reaction. We report the angularities of a zirconium oxide powder, before and after it has been treated with H_2SO_4 (*ca.* 0.25 mol l^{-1}). The decrease of about one order of magnitude in the angularity value is quantitative proof of the TEM evidence.

General relations

The SAXS intensities $I(h)$ (where $h = 4\pi\lambda^{-1}\sin\theta$, λ is the X-ray wavelength and 2θ is the scattering angle) can be expressed as follows for a spatially isotropic scatterer:

$$I(h) = 4\pi V\langle\eta^2\rangle \int_0^\infty r^2\gamma(r)\,\frac{\sinh r}{hr}\,\mathrm{d}r \qquad (1)$$

where V is the irradiated volume, r is the scalar distance between pairs of scattering centres, $\langle\eta^2\rangle$ the mean-square electron density fluctuation in the sample and $\gamma(r)$ the correlation function. For a system constituted by N different phases:[7]

$$\gamma(r) = 1 - \sum_{i<j}(n_i - n_j)^2 P_{ij}(r)/\langle\eta^2\rangle$$

where n_i is the constant electronic density of the ith phase and $P_{ij}(r)$, the so-called stick probability function, is the probability that r lies with one end in phase i and the other in phase j. Our samples can be considered isotropic two-phase systems, each phase having a uniform electron density. The two phases correspond to the void and to the bulk ZrO_2 (sample A) or to the ZrO_2 sulfate (sample B). The electron densities are, respectively, $n_2 \approx 0$ and n_1. It should be recalled that the $P_{ij}(r)$'s properties include:

$$\dot{P}_{ij}(0) = S_{ij}/4V; \quad i \neq j$$

$$\ddot{P}_{ij}(0) = -\alpha_{ij}; \quad i \neq j$$

where S_{ij} is the area of the surface which separates the ith phase from the jth one, while α_{ij} measures the angularity of the S_{ij} surface. The α_{ij}s cannot be negative and are positive only when edges and/or contact points are present on the S_{ij} surfaces. See ref. 5 and 6 for the explicit relation between the numerical α_{ij} value and the S_{ij} surface singularities.

Bearing in mind all the properties of the $P_{ij}(r)$s, the following parametrized correlation function is obtained:[7]

$$\gamma(r) = (1 + \mu)\exp(-\nu r)/[1 + \mu\exp(\nu r)] \qquad (2)$$

where $\mu \equiv (\sigma^2 - \alpha\phi)/\sigma^2$; $\nu \equiv (2\sigma^2 - \alpha\phi)/(\phi\sigma)$ and $\sigma = S_{12}/4V$, $\alpha = \alpha_{12}$, $\phi = \phi_1\phi_2$. We should recall that $\phi_i = V_i/V$ denotes the ith phase volume fraction. The relation between experimental intensity and angularity can be obtained explicitly from eqn. (1) and (2).

Experimental

Sample preparation

The ZrO_2 powders (sample A) were obtained by the hydrolysis with pure water of Zr propoxide, followed by calcination in air of the resulting amorphous hydroxide at 873 K. Sample B was obtained by surface sulfation of sample A with H_2SO_4 (*ca.* 0.25 mol l^{-1}).

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Small-angle X-ray scattering

The X-ray scattering of the powder samples was measured with a Kratky small-angle camera in the 'infinite slit' geometry, with an electronic step scanner. Ni-filtered Cu-Kα radiation with pulse height discriminator and proportional counter were employed. The intensities [denominated $J(h)$ for this geometry] were obtained from the time necessary to accumulate 10^5 counts for each scattering angle (2θ). The corrected intensities were obtained by subtracting the instrumental background intensity corrected for sample absorption. Finally, a contribution due to fluctuations of the electron density on a microscopic scale, was subtracted from the observed intensities so that a neat Porod plateau could be observed.[9]

Best-fit analysis

The values of parameters μ and ν are determined by requiring that

$$\chi^2 = \sum_{1}^{N} \{[J_{\text{exp}}(h_i) - J_{\text{th}}(h_i)]/J_{\text{exp}}(h_i)\}$$

be as small as possible. $J_{\text{exp}}(h_i)$ and $J_{\text{th}}(h_i)$ denote the ith experimental and theoretical intensities at the ith momentum-transfer value h_i

A PC 486 version of Marquardt's non-linear regression algorithm written in QUICKBASIC was used.[10]

Results and Discussion

When the SAXS intensities are multiplied by h^3, the comparison of the $J(h)h^3$ *vs.* h plots (Porod plot) relative to different samples gives a qualitative, but immediate, idea about the angularity of the systems. Greater values of the difference between the two areas $A_1 - A_2$ (the deviation integral) shown in Fig. 1 are related to greater values of the angularity.[3] This method could also quantitatively determine the angularity but, in most cases, exact knowledge of the limit $J(h)h^3$ value, as the momentum transfer h becomes infinitely large, prevents accurate determinations of the areas. In Fig. 2, the corresponding $J(h)h^3$ *vs.* h plots of sample A and B with their relative fits are reported. The experimental curves plainly show how the angularity of sample A is greater than that of sample B. The relative values of α obtained by the fitting procedure are, respectively, 8.00×10^{-5} Å^{-2} for sample A and 5.2×10^{-6} Å^{-2}) for sample B. Consequently, TEM results can be quantified as follows: using the procedure reported above, the sulfation of the crystalline particles of ZrO_2 provides an angularity decrease of about an order of magnitude. Since the ZrO_2 samples have the same monoclinic and tetragonal crystalline phases [only a small percentage (about 15 vol.%) of the latter phase is lost in the sulfate-doped samples as determined by a wide angle X-ray diffraction analysis of the sample[11]], and the porosity of the samples is close (76.5% for sample A and 71% for sample B), we may conclude that the difference in the α values should be mostly ascribed to an increase in the dihedral angles and to the shortening of the edges (it is recalled that an edge disappears when the corresponding dihedral angle approaches 180°). If ϕ_1 or ϕ_2 and d_B (the bulk density) are known, the α value can be expressed in m (g of sample)$^{-1}$ and the new values are 4.9×10^9 (sample A) and 3.37×10^8 (sample B).

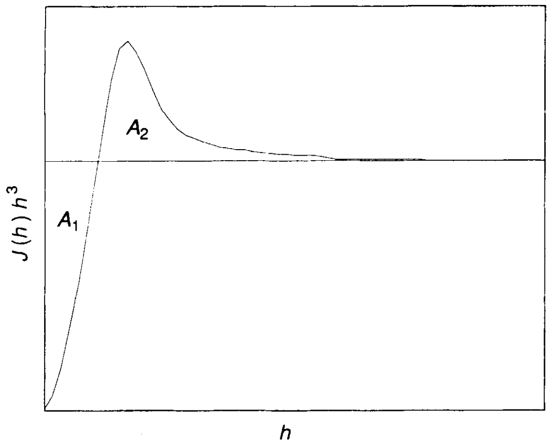

Fig. 1 Simpified example of the asymptotic behaviour of the scattering intensity

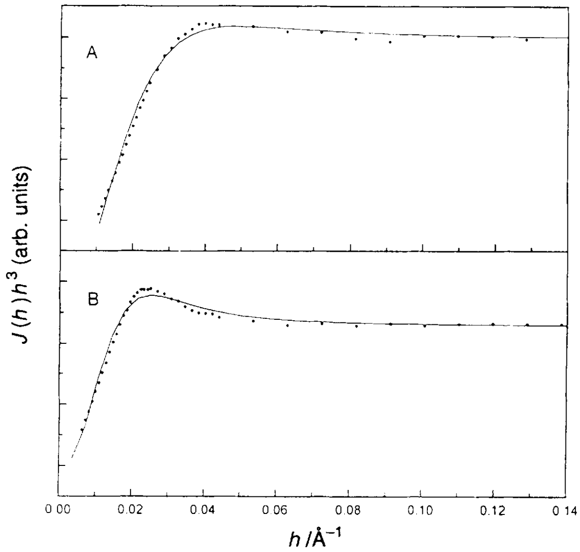

Fig. 2 $J(h)h^3$ *vs.* h. (····) Experimental intensities for the zirconium oxide powder, A, before and B, after it has been treated with H_2SO_4 (*ca.* 0.5 mol l^{-1}); (——) results of the best-fit analysis.

The aim of this short paper is to provide a suitable method to quantify the degree of smoothness of zirconia particles which, together the specific surface, may be used to obtain more detailed characterization of a porous system. We believe that further accurate measurements of the angularity of ZrO_2 samples prepared in different ways, and sulfated-doped with different reagents, could be very useful in clarifying some mechanisms of surface sulfation and morphological aspects of these nanostructures.

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