The Potential of Small-angle X-ray Scattering in Determining Nanoparticle Size Distributions

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Introduction

Small-angle x-ray scattering (SAXS) is a useful analytic technique for the study of aggregated nanopowders, such as fumed silica and titania. If a wide enough range of scattering angle is observed, the SAXS analysis results in a number of average features of such systems, including the primary particle size (radius of gyration), primary particle surface area, concentration, mass fractal dimension of the aggregates, aggregate size, and degree of aggregation. The features observed in SAXS can be converted to moments of a particle size distribution, $n_d(d_p)$, by careful consideration of the mathematical source of the parameters. For instance, the primary particle contrast is generally related to the squared volume of the particles and the sixth moment of the distribution [1]. This is similar to the moment obtained from the integrated intensity, or invariant. For a series of titania samples, we have compared the expected moments from SAXS with distribution functions obtained from particle counting of transmission electron micrography (TEM) micrographs. The potential of routinely reconstructing a log-normal particle size distribution, for example, from the SAXS moments is of great interest to the nanostructured powders community.

Methods and Materials

Co-flow diffusion flame aerosol reactors were used to flexibly produce nonagglomerated oxide nanoparticles with closely controlled characteristics. Fumed silica nanoparticles were made by oxidation of hexamethyldisiloxane (HMDSO) vapor in oxygen-methane single and double diffusion flames [2]. Nanostructured particles were made with specific surface areas of 35 to 155 m^2/g and 31 to 284 m^2/g for single and double diffusion flames, respectively, by controlling the oxidant flow rate. Nonagglomerated silica particles with d_p equal to 45-78 nm were made in both flame configurations when the flames were laminar, while in the transient to turbulent flames, the product particles were highly agglomerated. Increasing the oxygen flow rate in the single diffusion flame first decreases the specific surface area of the product powder and then continuously increases it with an increasing oxygen flow rate. In the case of the double diffusion flame, the powder's specific surface area first increases rapidly with an increasing oxidant flow rate and then continuously decreases with an increasing oxygen flow rate, since the flame becomes turbulent. Using methane as the carrier gas reduced particle necking that resulted in higher specific surface areas and nonagglomerated particles, as shown by SAXS even in turbulent diffusion flames.

The ultrasmall-angle x-ray scattering (USAXS) instrument on the 33-ID-D UNI-CAT beamline is uniquely suited for the study of nanoaggregates of silica and titania, since the primary particle size typically is on the order of 10 nm, while the aggregates grow to close to 1 µm in size. In order to determine the mass fractal dimension of the aggregates, it is necessary to observe small-angle scattering in the range q = 0.0001 to 0.001 $Å^{-1}$, which is inaccessible to pinhole SAXS as well as to static light scattering. The UNI-CAT facility is the only facility in the United States capable of observing this range with small-angle scattering. (Several such facilities are available in Europe and Asia.)

Results/Discussion

Figure 1 shows typical USAXS data from pyrolytic silica samples. The log-log plot of scattered intensity versus scattering vector q shows the average structural features of this system from about 1 nm to 1 µm. This is the widest q range available in the United States on a small-angle scattering instrument. The power of these data lies in the ability to fit such wide-ranging data and to develop structural relationships between the observed structural and scaling features of the material. The plot shows a typical fit to such data based on a mass-fractal aggregate model that describes, from low-q to high-q, the aggregate radius of gyration, low-q knee, mass-fractal dimension, intermediate-q weak power-law regime, primary particle size, high-q knee, and surface of the primary particles, highest-q power-law -4 decay (Porod's Law) [3-5].

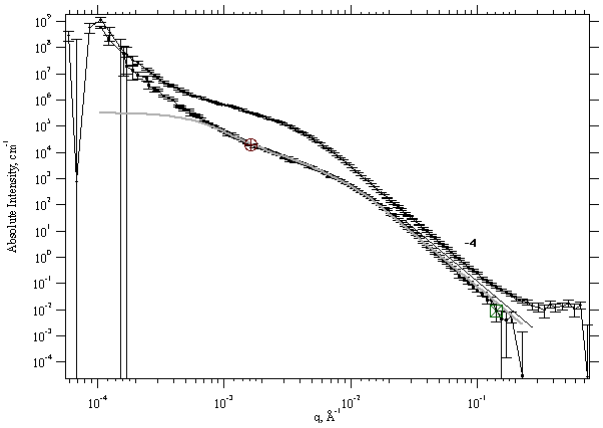

FIG. 1. Typical USAXS data for two pyrolytic silicas of different mass fractal dimension, low-q power-law decay, primary particle size, prominent knee in the data, and specific surface area, power-law -4 at high-q. Light curve is unified fit from using a UNI-CAT-developed user software package. (Fit range is shown by circle and square superimposed on data.)

From such fits, several scattering parameters are obtained that describe the average structure of these mass-fractal aggregates. For instance, one of these parameters is the radius of gyration for the primary particles. The radius of gyration is defined as follows:

$$\left\langle R_g^2 \right\rangle = \frac{\int_0^\infty n_p(d_p)\left[\int_0^\infty \rho(R)(R-R_0)^2 dR\right] d(d_p)}{\int_0^\infty n_p(d_p)\left[\int_0^\infty \rho(R) dR\right] d(d_p)}$$

where R_0 = the center of mass for the particles and ρ = the electron density. Traditionally, R_g is associated with the second moment of the particle size distribution.

Figure 2 shows a comparison of d_p calculated from R_g from assuming spherical primary particles [5] on the x-axis compared to d_p obtained from image analysis of TEM micrographs of the same samples. The TEM analysis typically took 10 h per sample, while the SAXS analysis was obtained in about 40 min, including data collection and data reduction from raw UNI-CAT data. Different moments of the TEM analysis are shown from the first moment to the sixth moment, including some fractional moments. Statistically, the best fit to the USAXS R_g is not the second moment, as expected, but the sixth moment of the primary particle size distribution. We are currently considering all of the moments obtained from SAXS and attempting to reconstruct particle size distributions on the basis of available moments from unified fits to USAXS data. Comparisons are also being made with differential mobility analysis data obtained on the same nanopowders. The UNI-CAT particle size distribution functions of J. Ilavsky are also being compared.

Acknowledgments

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References

[1] S. K. Friedlander, *Smoke, Dust and Haze, Fundamentals of Aerosol Dynamics*, 2nd Edition (Oxford University Press, New York, NY, 2000).
[2] H. K. Kammler, R. Mueller, O. Senn, and S. E. Pratsinis, AIChE J. **47**(7), 1533 (2001).
[3] G. Beaucage, J. Appl. Cryst. **28**, 717 (1995).
[4] G. Beaucage, J. Appl. Cryst. **29**, 134 (1996).
[5] J. Hyeon-Lee, G. Beaucage, S. E. Pratsinis, and S. Vemury, Langmuir **14**, 5751 (1998).

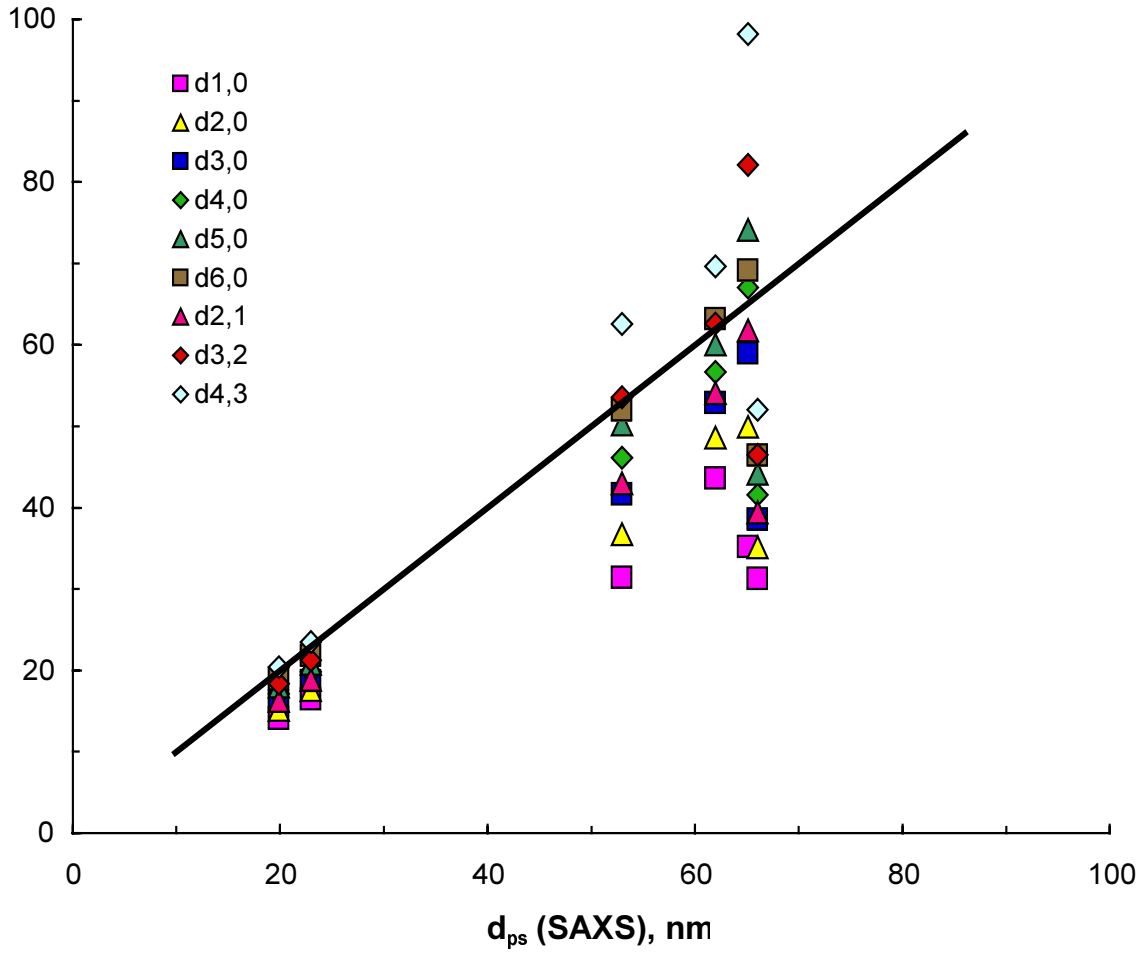

FIG. 2. Various moments of d_p for the primary particles from TEM analysis compared with d_p from USAXS data by using R_g from unified fits.