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SAXS investigation of porous nanostructures

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ABSTRACT

Fractal and aggregate structures of aerogels were investigated by small angle X-ray scattering in order to analyze the various evaluation methods of the SAXS data for porous nanostructures. Scattering data (SAXS, USAXS) for aerogels measured with laboratory equipment as well as synchrotron technique were interpreted in the terms of Guinier, Porod, Freltoft, Teixeira, and Emmerling theories. We modified the Freltoft fit in order to get information about the structure of elementary units. The performances of the evaluation programs were studied for different aerogels structures such as fractal of wide range, fractal of limited size, and aggregate systems. The evaluation of the scattering measurements resulted in fractal dimensions, sizes of the elementary units, sizes of the fractal domains or aggregates. Quality of the fits to SAXS data was characterized by a mathematical parameter and proved by TEM photography. TEM images confirmed the sizes of the elementary building units and clusters.

1. Introduction

The sol–gel process is one of the most practical and low energy consuming preparation methods for the synthesis of amorphous, porous materials. To preserve the structural features of the gel network and the inherent porosity of the wet gel samples, they have to be dried under supercritical conditions. Hereby, shrinkage of the monolithic body during drying is minimized and porous so-called aerogels are obtained. The analysis on porous structures of the aerogels is very important in respect of their application in the field of absorption, separation, and catalysis. In principle, the structural features of aerogels in the mesoscopic regime between 1 and 100 nm can be characterized with a variety of techniques. The mostly used one is the electron microscopy; transmission- and scanning-electron microscopy (TEM, SEM) providing direct images of the samples. The structure of ill-ordered materials, such as amorphous glasses, fractal systems, or aggregate structures is difficult to describe in direct pictures, these structures can well be characterized by scattering experiments. Small-angle X-ray scattering (SAXS) is non-destructive and gives the same information with high statistical accuracy due to the averaging over a microscopic sample volume.

The aim of the present work is to analyze the applicability and the limits of the scattering techniques applied for amorphous aerogels focusing on the nanometer sized features. The focus will be to compare the various evaluation models developed for the fractal and aggregate structures. Small-angle and ultra-small angle X-ray scattering (SAXS and USAXS), and transmission electron microscopy (TEM) have been used to determine the nanostructure of aerogels. Scattering data were obtained using several instruments such as laboratory equipment and synchrotron radiation sources and were interpreted in terms of Guinier [1], Freltoft et al. [2], Teixeria [3], and Emmerling et al. [4] theories and using the simple power-law expressions in Porod's region. The fractal systems of aluminosilicate and aggregate structures of silicate aerogel were studied in the experiments.

2. Experimental section

2.1. Preparation methods

Aluminosilicate gels (*samples 1 and 2*) were prepared in a one step procedure from tetraethoxysilane (TEOS) and an inorganic Al salt ($Al(NO_3)_3 \cdot 9H_2O$) in organic medium at 80 °C without

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catalyst. The chemical composition was 1 mol TEOS, 1 mol Al(-$NO_3)_3 \cdot 9H_2O$, and 20 mol 1-propanol. The gelation was performed by refluxing at 80 °C for 10–11 h [5]. *Silica* gels (*sample 3*) were synthesized from TEOS in 1-propanol in the presence of a base catalyst (NaOH). The composition of the initial solutions was 1 mol TEOS, 20 mol 1-propanol, and 1 mol NaOH. This mixture was heated at 80 °C for 3 h to get an optically clear wet silica gel.

The wet gels were dried under supercritical conditions. After washing with methanol, the gels were put into a steel autoclave and washed with liquid carbon dioxide for 2–3 days at 284 K, 6.0–7.0 MPa. After completion of the solvent exchange process, the temperature in the autoclave was slowly raised to 313 K, while the pressure was kept at 10 MPa. The supercritical carbon dioxide was slowly released from the autoclave by depressurizing to an ambient pressure during ≈20 h. After cooling to room temperature, opaque aerogel samples could be obtained.

2.2. Characterization methods

Small-angle X-ray scattering (SAXS) measurements were conducted on several instruments. The laboratory equipment was operated with a 12 kW rotating anode X-ray generator and a pinhole X-ray camera with variable distance (20.5–98.5 cm) from the sample to the two-dimensional detector (Bruker, AXS, Karlsruhe). The gels were covered in vacuum tight foil. The two-dimensional spectra were corrected for parasitic pinhole scattering, as well as for the foil scattering. X-ray scattering experiments were also recorded on the JUSIFA beamline of HASYLAB at DESY in Hamburg and on the BM2 beamline in the European synchrotron radiation facility in Grenoble. All the measured intensities have been normalized to a constant value of incident X-ray flux. USAXS measurements were performed on the BW4 beamline of HASYLAB at DESY, in Hamburg.

The *transmission electron microscopy (TEM)* investigations were performed on a JEOL 100 CX TEM with a tungsten filament operating at 100 kV in the bright field mode.

2.3. Evaluation of SAXS data

Different evaluation methods were used for the interpretation of the scattering data. The radii of gyration are determined from the Guinier-plot [1]. According to the calculations of Guinier, for aggregate systems consisting of small polydisperse particles, the scattering curve can be computed by the following formula:

$$I(q) = \frac{A}{(1+q^2r^2)^2}, \tag{1}$$

where q indicates the scattering vector, r is a measure of the particle radius, and $I(q)$ denotes the scattering intensity. If the aggregated particles form infinite fractal structures the formula might be written as

$$I(q) = S(q)\cdot P(q) = \frac{A}{q^\alpha}\cdot\frac{B}{(1+q^2r^2)^2}, \tag{2}$$

where $S(q)$ defines the structure factor of the arrangement of the particles, $P(q)$ is the single particle form factor, and α denotes the dimensionality of the fractally arranged system. In the case of porous systems, the radius of gyration (R_g) may denote the radius (r) of a particle, a pore, an aggregation, or a fractal domain.

$$r^2 = r_g^2 5/3. \tag{3}$$

Freltoft and independently *Teixeira* has developed an expression for relating the scattered intensity to the fractal structure of the aggregates [2,3]. It was assumed that the silica gels are built up from small, compact particles, which form finite fractal-like aggregates. The structure factor of the particle centers, $S(q)$, is related to the particle pair correlation function, $G(r)$, by Fourier transform:

$$S(q) = \int_0^\infty G(r)\frac{\sin(qr)}{qr}4\pi r^2 \mathrm{d}r. \tag{4}$$

For fractal-like aggregates of primary particles, *Freltoft* proposed the following expression for $G(r)$:

$$G(r) = \delta(r) + F\cdot r^{(D-3)}\cdot\exp(-r/\xi), \tag{5}$$

where $\delta(r)$ defines the Dirac delta function, F is a parameter describing the nearest neighbor correlations inside the aggregates, r means the radius of particles, D indicates the fractal dimension and ξ is the effective cut-off length describing the decay of the fractal-like correlations (due to the finite size of aggregates or their overlapping) [2]. The structure factor obtained by Fourier transform reads

$$S(q) = 1 + \frac{C\cdot\xi^D}{q\xi}\frac{1}{(1+q^2\xi^2)^{(D-1)/2}}\Gamma(D-1)\cdot\sin((D-1)\cdot\arctan(q\xi)), \tag{6}$$

where C is a constant. As can be calculated from the limiting behavior of $S(q)$ at $q = 0$, $B+1$ represents an average number of primary particles per aggregate, where $B = C(D-1)\Gamma(D-1)\xi^D$. The parameter ξ is connected with the gyration of the secondary particles [2,6]:

$$r_G = \sqrt{\frac{D(D+1)}{2}}\cdot\xi. \tag{7}$$

With the same assumptions, *Teixeira* also developed a formula that can also be applied for the evaluation of scattering data of fractal objects [3].

$$S(q) = 1 + \frac{D}{(qr)^D}\frac{1}{(1+1/q^2\xi^2)^{(D-1)/2}}\Gamma(D-1)\cdot\sin((D-1)\times\tan^{-1}(q\xi)), \tag{8}$$

where D indicates the fractal dimension, r is the radius of particles, ξ is a "cut-off distance", to describe the behavior of the pair correlation function at large distances [3].

Emmerling has upgraded and applied the expression of Teixeira for the evaluation of SAXS data for aerogels [4].

$$I(q) = V_o\phi(q)S(q)P(q), \tag{9}$$

where V_o denotes the volume of primary particles, $P(q)$ is the Debye function in this case, and $S(q)$ is derived from Teixeira assumption. The new component, $\phi(q)$ refers to the "concentration effect", i.e. close packing of nearly monodisperse clusters [4]. There are four parameters in the Freltoft formula, and only three in the Teixeira. On the other hand, if ξ is large compared to R, and the reciprocal of the measured smallest q limit, the denominator of the Freltoft fit becomes large, as well as it is equal to $(qR)^D$ in the Teixeira model. This fact enlarges the difficulties of the calculation of ξ by Teixeira.

The Emmerling expression can be reduced, if the upper-limit length-scale for the mass fractal domain (ξ) is taken to be infinite. An infinite size of a fractal object can be taken into account if the size of fractal domain is out of the scattering q-range. The simplified Emmerling–Fratzl formula [7]

$$S(q) = 1 + \frac{D\Gamma(D-1)\sin[\pi(D-1)/2]}{(qR)^D}. \tag{10}$$

Pedersen and Mortensen have written an expression for the estimation of the cluster–cluster correlation length [8]. The fractal dimensions can be obtained from the slope (μ) of SAXS curves in the Porod's region using a simple power-law expression; $I(q)\sim q^{-D}$ [9,10]. Schaefer et al. dealt intensively with the evaluation of SAXS