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USAXS AND X-RAY MICROSCOPY INVESTIGATIONS ON SILICA AND PRECURSORS OF ZEOLITES

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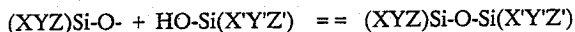
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ABSTRACT

Combination of SAXS and USAXS measurements provide an extended q-range (0.006-3.0 nm⁻¹) to study fractal growth of both aging silica gel as well as precursors of zeolite-A. Mass (silica) and surface (zeolite) fractals are observed. Scanning transmission X-ray microscopy (STXM) proves to be an extremely useful technique to obtain direct images of wet samples in the 0.1-100 micron range, confirming the SAXS/USAXS results on even larger length scales.

INTRODUCTION

Silica and silica gels are important industrial raw materials. The majority of the processes for silica and silica gel production is based on the acidification of water glass, inducing condensation (polymerization) reactions between silicon tetrahedra:



with X,Y,Z,X',Y' and Z' hydroxy or silicic (both monomer and polymer) groups. Due to the tetrahedral-directed bonds ring- and cluster-shaped polymers are favoured resulting in spherical elementary particles [1]. These particles may combine to aggregates [2,3], analogous to the well-studied aggregates formed by hydrolysis of alkoxy silica's; see [4,5] and references cited herein. At sufficient silica concentration the growing aggregates will be interconnected resulting in a network, the gel. This often very fragile network is strengthened during aging. By hydrolysis and condensation reactions silica is redistributed, with dissolution preferably on the periphery and precipitation in the crevices and "necks" of the aggregates [1].

Aging is of crucial importance to the texture of silica. For example, only after aging is the geleeous network strong enough to avoid collapse when water is removed by drying, resulting in a mesoporous solid [6]. Because the hydrolysis/condensation reactions are catalyzed by OH⁻ ions [1,7], the presence of cations and organic templates with polar groups is expected to have a strong influence on the aging processes, analogous to the selectivity in dissolution of silica as shown by NMR [8,9].

During the preparation of zeolites [10] the conversion of the starting silica or silica-alumina gel to the precursors of crystalline zeolites can be considered as an aging process. Investigations on the changing gel structure during aging are necessary to understand the fundamental steps, especially the relations between reaction conditions (pH, concentrations, temperature), addition of cations or templates and the resulting zeolite structure. Recently, scattering by light, X-rays (SAXS) or neutrons (SANS) has proven to be very efficient at providing information concerning the distribution of mass on colloidal scale, irrespective of the phase (solution, sol, gel or

amorphous solid) one is dealing with [4,5,11,12]. Exploitation of the fractal properties of aggregates is very helpful in the interpretation of scattering data. Due to the power-law mass density distribution in fractals, from a log-log plot of scattered intensity I versus scattering vector q , the size (radius of gyration) of the fractal aggregates, the size of the primary particles and the fractal dimensionality can be extracted [12].

However, a serious limitation to obtaining the necessary data stems from the often very large q range exhibited by fractal aggregates (in diluted systems up to three decades [11,14]). Combination of SAXS (SANS) and light scattering has been applied [4,11,15] but this last method can not be used for opaque systems (aged silica gels, zeolites). We have chosen an alternative solution: extending X-ray scattering to very small angles. With USAXS (Ultra Small Angle X-ray Scattering) using the synchrotron source at Daresbury the 1-50 nm range of SAXS might be extended to 1000 nm [16,17]. In this paper we show that the SAXS-USAXS combination may be a good alternative for light scattering and SAXS/SANS.

Although the physical basis and the interpretation of scattering spectra from fractal systems is well understood, we are still dealing with an indirect method. A "second opinion" using a direct imaging technique (e.g. microscopy) would give a very valuable confirmation and expansion of the information obtained by scattering. Conventional electron microscopy can not be used because it destroys or changes the tenuous and fragile aggregates by the forced removal of water in the high-vacuum system. A possible solution might be cryo-electron microscopy: extremely fast cooling of the sample preserves the structure of a gelled Ludox sol in the vitreous ice [18].

X-ray microscopy using photons with energies in the range 100 eV to 1 keV fills a niche between optical and electron microscopy [19,20]. The short wavelength of x-rays means that sub-optical resolution can be achieved in specimens that need not to be optically transparent. The dominant beam-specimen interaction is photo-electric absorption which results in elemental contrast even from materials containing adjacent elements in the periodic table; most low atomic number elements have a K or L absorption edge in the soft x-ray region. The possibility to examine species under atmospheric conditions combined with the choice of x-rays in the "water-window" energy range (277-525 eV) is not only attractive for examination of biological material in an aqueous medium, but also very promising for solutions or gels of silicas and zeolites. However, it is only recently that technology has developed sufficiently to allow the manufacture of Fresnel zone plates for use as diffractive focusing elements. In addition, the advent of synchrotron radiation has now provided a sufficiently intense tunable source of radiation in the soft x-ray regime, resulting in the design of several different x-ray microscopes. The King's College scanning transmission x-ray microscope (STXM) was first used on the Daresbury synchrotron radiation source (United Kingdom) in the summer of 1986 and during the past years modifications and improvements have been made [21]. In this paper some results obtained on silicas and zeolites are described, in combination with SAXS-USAXS experiments.

EXPERIMENTAL

Water glass was obtained by dissolution of Aerosil 380 (Degussa) in KOH (Merck,p.a.). Silica gel was prepared by addition of water glass to 1.0 or 0.1 M HCl until pH = 4.0.

Zeolite-A was prepared by addition of a water glass solution (24.7 g water glass (Merck, 27% SiO₂), 2.5 g NaOH, 33.3 g H₂O and 4.85 g SiO₂ (Aerosil 200, Degussa)) to a alumina solution (18.2 g sodium aluminate (Riedel-De Haen; 54% Al₂O₃), 5.2 g NaOH (Merck,p.a.) and 236 g H₂O) and heated at continuous stirring at 80°C during

24 hours. To avoid progress in reaction during the measurements (SAXS, USAXS, X-ray microscopy) samples from the reaction mixture were cooled down to room temperature.

SAXS spectra were measured using synchrotron radiation ($\lambda = 0.154$ nm) at station 8.2 at Daresbury Laboratories (United Kingdom). For both solutions and gels cells were used with mylar windows and 1 mm pathway. Spectra were corrected for background and parasitic radiation and checked by extrapolation to $q \rightarrow \infty$ in $I \cdot q^{-4}$ or $I \cdot q^{-D}$ plots [22, 23].

USAXS spectra were measured with the Bonse-Hart twin crystal diffractometer system on station 2.2 at Daresbury Laboratory [16, 17]. Assuming infinite slit smearing for the Bonse-Hart system the fractal dimension is determined by adding -1 to the negative value of the slope in $\log(I) \cdot \log(q)$ plots [24].

X-ray imaging has been performed with the King's College scanning transmission x-ray microscope (STXM) using soft x-ray photons ($\lambda = 3.28$ nm) from station 5U2 at the Daresbury Laboratories [19-21]. Images were taken of diluted reaction mixtures from aging silicas or zeolitic precursors. Before scanning, samples were superficially dried (as confirmed by IR-spectra) by exposing small droplets to the air.

RESULTS

To compare the SAXS and USAXS data in figure 1 curves are shown of representative samples of aging silica and precursors of zeolite-A. Because the original spectra showed large differences in scattered intensity, in figure 1 arbitrary intensity units have been chosen and the curves have been shifted along the vertical axis.

The SAXS curve of silica is representative of an aging silica gel [2,6,14]. The growth of the endpoint of the straight line (with constant fractal dimension, $D = 1.90$), corresponding to the growth of the radius of gyration of the fractal aggregates, did already surpass the low q boundary (0.3 nm^{-1}) at these concentrations after a few minutes, resulting in a straight line over the full q -range during further growth, gelation and aging.

With USAXS the q -range is extended to $q = 0.006 \text{ nm}^{-1}$. However, because the Bonse-Hart camera is a scanning system with scanning times in the order of hours, only stable systems (silica in the aging stage, "frozen" zeolitic precursors) can be studied. In figure 1 the USAXS spectrum of an aged silica is shown. Due to the relatively low silica concentration and the extremely high background scattering at the (ultra)low q values, this spectrum showed a rather poor intensity/background ratio. The only reliable feature to extract from this spectrum proved to be the straight slope, indicating an extended fractality of the aggregates. However, the fractal dimension could not be determined accurately, due to low intensity/background ratio. In figure 1 the USAXS curve has been drawn tentatively assuming the same fractal dimension as found for the SAXS curve ($D = 1.90$).

Contrary to silica gel samples of the zeolite-A reaction mixture showed the presence of surface fractals with $D = 3.6 - 3.7$. Only after 7 hours, when by x-ray diffraction in the reaction mixture the presence of small quantities of crystalline zeolite-A could be demonstrated, the fractal dimension approaches $D = 4$, indicating advancing aging prior to crystallization. Due to the high scattering in the (high silica) zeolitic samples, the intensity/background ratio was much more favourable in the USAXS spectrum, so a reliable $\log(I) \cdot \log(q)$ plot and fractal dimension could be obtained. Small differences between fractal dimensions in the SAXS and USAXS

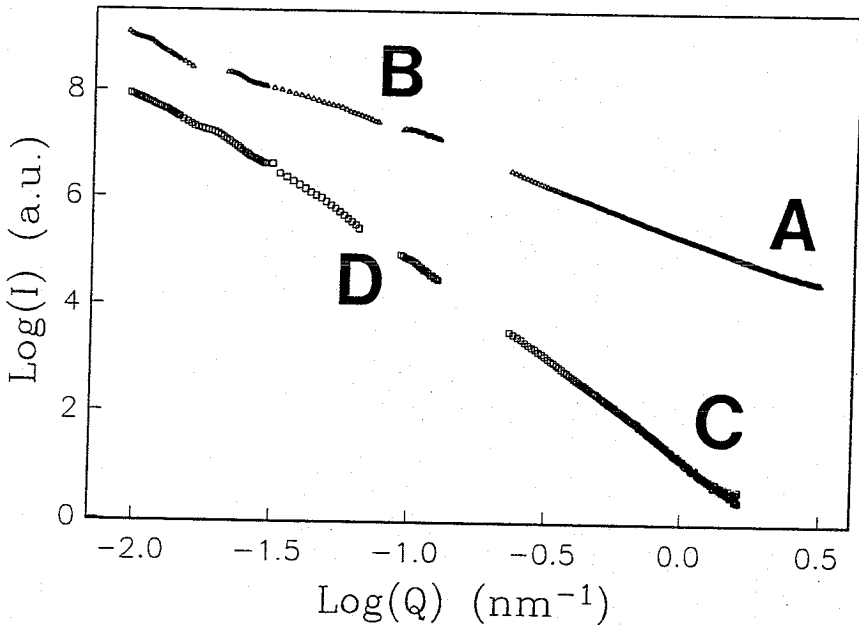


Figure 1. SAXS and USAXS curves of aged silica (A and B) and reaction mixtures of zeolite-A (C and D).

spectrum can be attributed to different samples and different background correction.

The striking difference between the mass and surface fractals of the silica gel and the zeolitic precursor respectively are confirmed by scanning transmission x-ray microscopy (STXM) (figure 2). The (diluted) aged silica shows typical fractal aggregates with high anisotropy as may be expected from reaction-limited cluster-cluster aggregation [25]. Moreover, the fractal range extends even into the micron range, adding another decade to the fractal range of (diluted) silica aggregates. However, one has to be careful because the radius of gyration (indicative of the fractal range in SAXS or USAXS spectra) is much less than the size of the anisotropic aggregates shown in the STXM images. Because the projection of a three-dimensional aggregate to two dimensions will not effect the value of the fractal dimension D for values of D less than 2 [26-28], a rough indication of the fractal dimension of the aggregates may be obtained by applying the relation between mass and radius in fractal systems ($M = a \cdot R^{-D}$) on STXM images. The resulting D values (1.55 - 1.7) are lower than expected, but may be attributed to dilution effects.

The images of the precursor gel of zeolite-A show aggregates of spherical particles. The radius of gyration of the spherical particles has the order of magnitude of 1 micron. According to USAXS the particles behave as surface fractals.

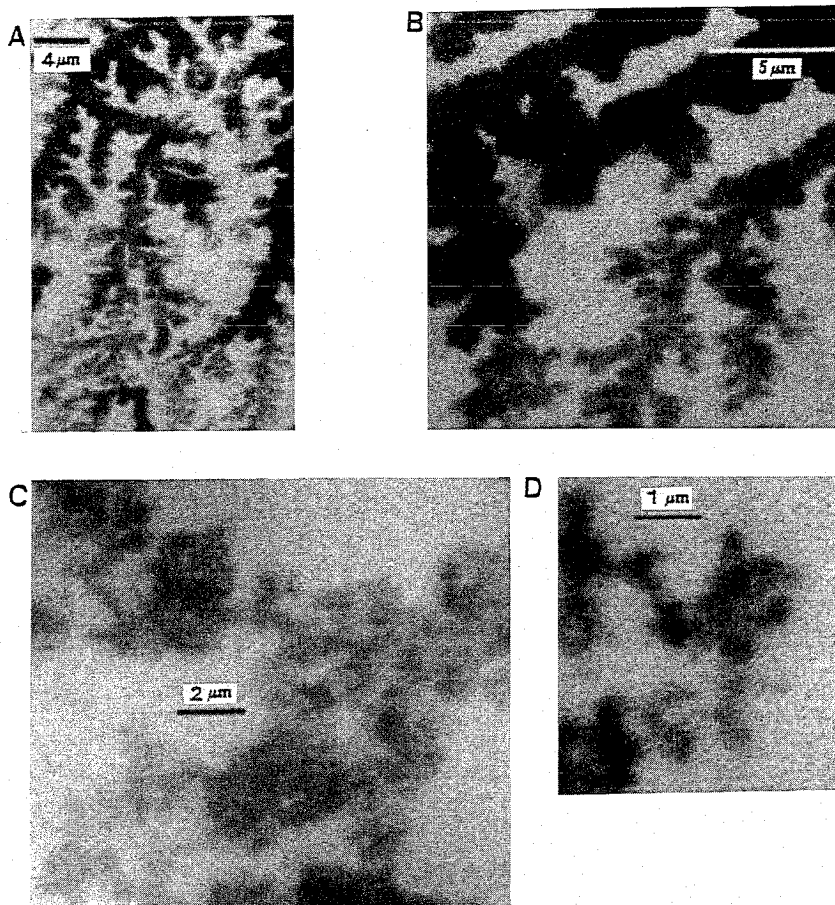


Figure 2. STXM images of diluted solution of aged silica (A and B) and diluted reaction mixture of zeolite-A (C and D).

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